U.S. DEPARTMENT OF COMMERCE
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PB-293 278

Environmental Assessment of Coke By-product Recovery Plants

Research Triangle Inst, Research Triangle Park, NC

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, NC

Jan 79

PB 293278

United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

EPA-600/2-79-016
January 1979

Research and Development

EPA

Environmental Assessment of Coke By-product Recovery Plants

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SPRINGFIELD, VA. 22161

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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-79-016

2.

3. RECIPIENT'S ACCESSION NO. PB293278

4. TITLE AND SUBTITLE Environmental Assessment of Coke By-product Recovery Plants

5. REPORT DATE January 1979

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S) D.W. VanOsdell, D. Marsland, B.H. Carpenter, C. Sparacino, and R. Jablin

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, North Carolina 27709

10. PROGRAM ELEMENT NO. 1AB604C and 1BB610C

11. CONTRACT/GRANT NO. 68-02-2630, Task 1

12. SPONSORING AGENCY NAME AND ADDRESS
EPA, Office of Research and Development
Industrial Environmental Research Laboratory
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED Task Final; 3/77 - 6/78

14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Robert V. Hendriks, Mail Drop 62, 919/541-2733.

16. ABSTRACT The report gives results of an initial screening study, initiating a multimedia environmental assessment of coke by-product recovery plants in the U.S. The study included both the gathering and analysis of existing data and sampling and analysis at one plant based on EPA's Industrial Environmental Research Laboratory-RTP Level 1 protocol. Process data concerning design and operation of existing plants and processes were examined. Many variations of all process types exist, forcing an examination of the industry to determine the commoner processes. Sampling and analysis utilized a basic EPA Level 1 format, tailored for organic vapor sampling. Specific samples were also analyzed for cyanide. Air was sampled at all suspected pollution sources, most of them storage tanks. The largest single source was the final cooler cooling tower: aromatics at > 50 g/Mg coke and cyanide at 278 g/Mg coke were both significant. Polynuclear aromatic hydrocarbon (PAH) compounds were indicated, but not quantified. Concentrations of pollutants in the vapor above storage tanks were measured, but actual emission rates were not determined because of the difficulty in measuring working and breathing losses for the tanks sampled. Water sampling data from the same plant, developed by EPA's Effluent Guidelines Division, were included in the overall study analysis.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Cyanides	Pollution Control	13B	07B
Coking	Aromatic Polycyclic Hydrocarbons	Stationary Sources	13H	
Sampling		Organic Vapors	14B	
Analyzing				
Assessments				
Organic Compounds			07C	

18. DISTRIBUTION STATEMENT Unlimited

19. SECURITY CLASS (This Report) Unclassified

20. SECURITY CLASS (This page) Unclassified

21. NO. OF PAGES 387

22. PRICE PC A17 MF A01

EPA Form 2220-1 (9-73)

EPA-600/2-79-016
January 1979

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Contract No. 68-02-2630
Task No. 1
Program Element No. 1AB604C and 1BB610C

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

PREFACE

This report was prepared for the Environmental Protection Agency to present the results of work performed under Contract No. 68-02-2630, phase 1. Mr. Robert V. Hendriks served as EPA Project Officer.

The research was conducted in the Energy and Environmental Research Division and the Analytical Sciences Division of the Research Triangle Institute. Mr. Ben H. Carpenter, Head, Industrial Process Studies Section, served as Program Manager. Mr. Douglas W. Van Osdell was the principal investigator. Dr. Charles Sparacino directed the chemical analysis effort. Mr. Richard Jablin, Jablin Associates, provided engineering assessment effort. Dr. David Marsland provided state-of-the-art process technology appraisal. Mr. Walter S. Smith, Entropy Environmentalists, directed the plant sampling effort. Dr. Denny Wagoner directed Level 1 field chemical analyses.

ABSTRACT

The objective of this work was to perform a multimedia environmental assessment of coke by-product recovery plants in the United States. The project included both gathering and analyzing existing data and the development of needed information through a sampling and analysis program based on the EPA Level 1 protocol.

Existing sources were searched and process data concerning design and operation of existing plants and processes were examined. Many variations of all process types exist, forcing an examination of the industry to determine the more common processes. No data were available on many sources and a sampling plan was developed.

The sampling and analysis program was a basic EPA Level 1 format tailored for organic vapor sampling. In addition, specific samples were analyzed for cyanide. The samples were mostly of the vapor above storage tanks, with additional samples at the locations deemed most important. Rates were determined where measurable. Storage tank emissions could not be quantified, with one possible exception. With respect to air emissions, the single largest source was the final cooler cooling tower; both aromatics at greater than 50 g/Mg coke and cyanide at 278 g/Mg coke were significant. PNA's were not quantified, but were indicated. Concentrations of pollutants in the vapor above storage tanks were measured, but actual emission rates were not determined because of the difficulty of measuring or estimating working (due to changing product levels) and breathing (due to atmospheric pressure changes, temperature changes, etc.) losses for the tanks sampled. Water sampling data from the same plant, developed by EPA's Effluent Guidelines Division, were included in the overall study analysis.

This report was submitted in fulfillment of Contract No. 68-02-2630 by Research Triangle Institute under the sponsorship of the U.S. Environmental Protection Agency, and covers the period March 1, 1977, to June 30, 1978.

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1.0 SUMMARY

This report discusses the findings of a screening study of the multimedia environmental effects of U.S. coke by-product recovery plants and their related pollution control technologies. The purpose of the study was to analyze relevant background data, to acquire new data by sampling and testing, and to draw conclusions concerning the environmental acceptability of the process.

There are 60 coke by-product plants in the country; these processed gases from an estimated 75 million metric tonnes of coal in 1975, the latest year of record. Table 1 lists 42 pollutant sources for the by-product recovery plant. These are related to eight major operations; tar processing, ammonia processing, dephenolization, final cooling-naphthalene handling, light oil recovery, desulfurization, cyanide handling, and water handling. For each operation there are alternative technologies and existing plants employ only a few of the thousands of combinations of operations available.

The table identifies the scope of pollutant emissions information developed during the study, by indicating whether sampling was done (x); sampling was not done, but data are available (y); or sampling was not done and data are not available (z). Types of pollutants to air, land, and water are indicated.

Except for still vents and forced drafts (e.g., final cooler cooling tower), emissions to air are fugitives--tank breathing and working losses, open decanters, and basins. Fugitives are also due to faulty equipment, such as pump seal leaks and flange leaks, but these are not addressed. Pollutants identified include light aromatics (LA), polynuclear aromatics positively identified (P), and polynuclear aromatics indicated (PI).

Light aromatics were predominantly benzene and its homologs. Estimated emission factors for these pollutants, derived from sample data from one plant, are given in Table 2. This table is based on 1 tonne (1000 kg) of coal fed to the ovens. Nine sources were investigated, seven by sampling.

TABLE 1. COKE BY-PRODUCT RECOVERY PLANTS POLLUTANT SOURCES

Operation Emissions Source	Pollutants to:		
	Air	Water	Land
Tar Processing			
tar decanter	(x),f,P,LA,H_2S		(y),sludge
prim. cooler condensate tank	(x),f,NO,LA,H_2S		
tar dewatering and storage	(x),f,P,LA		(z),tar product
tar topping (distillation)	(y),f	(z),bar cond.	
tar distillation-product	(x),f,PI,LA		
tar distillation pitch			(y),pitch product
Ammonia Processing			
excess liquor tank	(z), f		
excess ammonia liquor	(x),P,LA		
phenol extraction	(z),f		(z),sludge
ammonia stills	(z),vent		
fixed still			(y),sludge
sulfate crystallizer-dryer	(z),f		
sulfuric acid storage tank	(z),f		
ammonium sulfate storage	(z),f		
Dephenolization	(y),f if vented to gas main	(z)	
Final Cooler, Naphthalene Handling			
cooling tower, for contact cooler	(x),P,HCN,LA		
hot and cold wells		(x),P,LA	
naphthalene separator (froth floatation)	(x),f,PI,LA		
naphthalene dryer	(y), vent	(z),water decanted	
Light Oil Recovery			
wastewater		(y)	
wash oil sludge			(y)

TABLE 1. (continued)

Operation Emissions Source	Pollutants to: Air	 Water	 Land
wash-oil storage	(z),f		
wash-oil decanters	(z),f		
light-oil storage	(x),f,LA,H_2S		
light-oil condenser vent	(z)		
Desulfurization			
by absorption		(y),absorption purge	
by wet oxidation		(y),absorption purge	
Cyanide Handling			
catalytic destruction			
waterwork	(z)		
regenerate or blown air			
ammonium polysulfide		(z)	
Coke Oven Gas, After Tar Removal		(x),C_1-C_6,LA,H_2S	
Biological Treatment Plant			
Feed		(x),Ph,P,LA,CN,Cl,SO_4,SCN	
effluent	(y)	(x),Ph,P,LA,SCN,CN,Cl,SO_4	
sludge			(x),Fe,Cl,Mg,F,Si,Al,etc. present
			(x),aliphatics,phenolics,sat. HC present
Plant Atmosphere			
Downwind-Upwind, concentration increase	(x)	(x),HCN:0.05-0.06 vppm	

Ph = phenols
LA = light aromatics (benzene, etc.)
NO = no organics sample
PI = polynuclear aromatic compounds may be present
P = polynuclear aromatic compounds present

f = fugitive
S = sludge
(x) = sample taken
(y) = sample not taken, but data available
(z) = sample not taken, data not available

TABLE 2. ESTIMATED POLLUTANT EMISSIONS RATES, BASED ON INDICATED AND CONFIRMED SPECIES FOUND IN SAMPLES TAKEN AT ONE COKE BY-PRODUCT PLANT

Operation Emission Source	Rate: scm/tonne of coal	Temp. °C	Analysis Level		Emission Rates, g/tonne of coal[f]										Effluent state
			1	2	Benzene	Toluene	Xylene[b]	PNA[c]	Specific PNA's quantified	Sulfur compounds[g]	Cyanides[h]	NH_3	Phenol	Lt. oil	
Tar Processing															
decanter	1.5(3)[a]	76	x	x	15.6	1.1	0.3	4.1[d]	Biphenyl, 0.03; quinoline, 0.06	9.1	ND[e]				Vapor
sludge, pitch[i]	0.07[k]														Liquid
dewatering-storage	0.1(5)	29	x	x	0.006	0.002	0.0016	0.003	Biphenyl, 0.002; quinoline, 0.0006	NTD	ND				Vapor
prim. cooler condensate tank	1.2(3)	62	o		6.3	0.8	0.3	ND	None[o]	3.9	ND				Vapor
topper (distillation)[i]															
distillation product storage	0.02	50	x		0.004	0.003	0.002	0.011		ND	ND				Vapor
Ammonia Processing															
excess liquor tanks[i]	102 l/tonne				Amounts of organics are counted in the wastewater						6.1[l]	611	148		Liquid[p]
excess ammonia liquor															
bar. conden. water, sulfate dryer[i]															
lime-leg sludge	0.5 kg/tonne														
other sources[i]															
Dephenolization[i]															
Final Cooler, Naphthalene Handling															
cooling tower for contact cooler	2306	Ambient			35.9	NTD	NTD	6.4	Biphenyl, 0.06; quinoline, 0.32	7.6	212				Vapor
naphthalene separator[m]	Not known	Ambient	x												Vapor
naphthalene dryer	2.1	101			Grab sample results not satisfactory for estimates										Vapor
Light Oil Recovery															
wastewater[j] (wash oil, sludge)[i]	70 - 360 l/tonne										0.4 - 0.7	0.4 - 1.1	0.6 - 1.9	2.1 kg/t	Liquid[p]
wash oil storage and decanter[i]															Vapor
light oil storage	11.1	50	o		11.6	0.4	NTD			0.5					Vapor
wash oil sludge[i]															
Wastewater															
biotreatment plant effluent	335-900 l/tonne				0.12 - 0.13			0.3 - 0.7[q]			14	65	1.1	7.8 g/tonne	
biotreatment plant sludge	1.2 kg/tonne							0.007							
Total, all sampled sources	g/tonne				69.5	2.3	0.6	11.2		21.1	226	65	1.1	7.8	
	kg/day, for 5,142 tonne coal				357	11.8	3.1	57.6		108.5	1162	334	5.6	40.1	

a Estimated as working loss from the number of units shown in ( ).
b Xylene plus ethylbenzene
c Polynuclear aromatics are assumed to be equal to the GRAV content of the effluent
d Major component = naphthalene
e ND = not determined
f Tonne = 1,000 kilograms coal
g Sulfur compounds, as H_2S
h Cyanides as HCN
i Not sampled
j NTD = not detected
k Liters per tonne of coal
l From Dunlop and McMichael
m Emission rates are unknown. Toxicity data are shown in Table 3
o Level 1 sampling, in part. No XAD-2 resin sample
p Stream is processed in the biotreatment plant
q Estimate based on identified PNAs

For the sources investigated, the daily total emissions from processing 1.8 million cubic meters per day of coke oven gas are estimated to be:

Light aromatics (mostly benzene),	372 kg/day
Polynuclear and high boiling aromatics (PNA)	57.6 kg/day
Sulfur compounds	108 kg/day
Cyanides	1,162 kg/day
Ammonia	334 kg/day
Phenols	5.6 kg/day
Light oils	40.1 kg/day

These data were developed utilizing methodologies based on the Environmental Protection Agency's Level 1 protocols,[58] with limited gas chromatograph-mass spectrometer identification of specific pollutants. These quantities are subject only to uncertainties in emission rate estimates, sampling and testing areas. The PNA's shown are the quantities of residual organics obtained upon evaporation of the solvent used for extraction, which are nominally those organics with boiling points above 300°C. The PNA's emission factors are subject to the additional uncertainty inherent in this method of estimation. Specific PNA's were not identified except for three sources considered most likely to involve them: the tar decanter, the dewatering and storage tanks, and final cooler cooling tower. Sulfur compounds are reported as hydrogen sulfide; cyanides, as hydrogen cyanide.

Light aromatics, the predominant emissions, were found in the highest concentration in emissions from the tar decanter, the primary cooler condensate tank, the naphthalene separator, the light oil storage tanks, and the distillation product storage tanks. PNA's (as total non-evaporables) concentrations were highest at the following sources: wastewater treatment sludge tar decanter, tar dewatering and storage, tar distillation products, naphthalene separator, final cooler cooling tower, and water from the biological treatment plant. Cyanide concentrations were highest at the final cooler cooling tower and in the effluent from the biological treatment plant. Sulfur compound concentrations were highest at the tar decanter, the primary cooler condensate tank, the naphthalene separator, the light oil storage tanks, and in the plant wastewater effluent.

The data suggest that the PNA's accumulate as a concentrate in the liquid streams (tars, flushing liquor, tar products, wash and wastewaters). PNA's accumulated in the water from the final cooler reentered the air as the recycled water passed through the open cooling tower.

Ambient air samples, taken upwind and downwind of the by-product plant, showed increases in both benzene and cyanide concentrations. The following results were obtained:

	Hydrogen Cyanide (volume ppm)	Benzene (volume ppm)
Downwind	0.062	0.8
Upwind	0.006	0.6
Gain	0.056	0.2
Toxic units/scm	toxic units/scm	toxic units/scm
Downwind	0.0062	0.9
Upwind	0.0006	0.7

These results indicate that cyanide concentrations downwind of the by-product plant were well below the environmental goal. Cyanides of this plant were more a problem in wastewaters than in the air. Downwind benzene concentrations, on the other hand, were close to the goals.

Of the 42 pollutant sources listed, all but fifteen (marked z in Table 1) have been examined. Six of the fifteen were in the ammonia processing operations, which the plant studied considered to be proprietary. The sludge from the lime leg of an ammonia still would be produced at an estimated 0.35 kg/Mg of coke. The extent to which PNA's are entrained in this sludge has not been reported. The acid storage and ammonium sulfate drying and transport operations are expected to have very low pollutant discharges to any medium.

The remaining nine unstudied sources are the wash oil storage, decanters, and condenser vents of the light oil recovery operations, the decanted water from the naphthalene dryer, the wastewaters from dephenolization, the tar-topping barometric condenser, and the cyanide handling processes, some of which are an inherent part of desulfurization operations. The wastewater streams involved in these operations were sent to a combined wastewater treatment plant at the study site.

Alternatives to the removal of ammonia as ammonium sulfate include the production of anhydrous ammonia and incineration of the separated ammonia. Cost comparisons for the handling of 1.4 million cubic meters of gas per day indicate that incineration is the alternative with the lowest annualized cost even after credits are taken for the sale of products obtained using the other processes. However, the environmental effect of ammonia incineration has not been determined. The production of anhydrous ammonia can be economically attractive, however, if the coke plant is large enough and the entire by-product plant is designed to favor this product.

Dephenolization of ammonia liquor by coke oven light oil, followed by reaction with sodium hydroxide to produce sodium phenolate for sale appears to be more costly than dephenolization by activated sludges. The latter treatment may be necessary in either case in order to meet effluent pollutant limitations.

A great deal of research, development and regulatory effort is being expended on desulfurization processes. Those in use include Dravo/Still, Sulfiban, Vacuum Carbonate, Stretford, Cryogenic, and Takahax. Compared with the first three, the Stretford process has the lowest annualized cost at $1.97/1,000 scm of gas treated, although the Dravo/Still process at $2.05/1,000 scm is only slightly more expensive.

Certain pollutant-control technologies appear to have potentially broad application within coke by-product plants. The blanketing of holding tanks with coke oven gas originally used in the light oil recovery process to exclude air and prevent the buildup of sludges, eliminates the tank vents as an emissions source. The blanketing gas is vented back into the main gas stream. This technique could perhaps be applied to many sources even to refined benzene tanks, if the gases were first desulfurized to prevent deteriorization of the product. Problems to be addressed in considering the broader use of blanketing include making provision to admit the flammable gas into the various operating areas, and to prevent the condensation of naphthalene.

The collection of napthalene in open vessels inherently causes emissions of naphthalene along with other organic pollutants contained in the process streams at this stage. Tar bottom final coolers should keep much of the organics in the tar. This combined with a closed cooling cycle, should reduce substantially the emissions from the final cooler.

The relative environmental impact of some of the pollutant sources within the by-product coke plant is addressed in Table 3. The biological treatment plant effluent is the most significant of the by-product plant

TABLE 3. NORMALIZED RELATIVE HAZARD OF BY-PRODUCT COKE PLANT POLLUTANT SOURCES

	Normalized Relative Hazard
Tar Decanter Vapor	0.036
Tar Dewatering/Storage Vapor	≈0
Primary Cooler Condensate Tank Vapor	0.017
Distillation Product Storage	0.001
Cooling Tower for Contact Final Cooler	0.349
Light Oil Storage Vapor	0.028
Biotreatment Plant Effluent	0.434
Biotreatment Plant Sludge	0.135

sources. This was due to a combination of a large effluent rate and the sensitivity of the impact measurement to organic pollutant concentrations. The other major sources are the cooling tower for the contact final cooler and the biological treatment plant sludge.

The procedure used to arrive at Table 3 uses a weighting process which considers pollutant concentration, hazard in the proper media, and emission rate. For the by-product plant, the weighting factors reflecting the great hazard of certain PNA's essentially controlled the results. The procedure is explained fully in Section 6.10. Weighting factors were obtained from the Multimedia Environmental Goals.[60]

This study is a limited-scope first look at the by-product plant from the environmental point of view. As such, it points to a need for control of light aromatics and PNA's. Control may be most likely achieved through techniques that essentially eliminate the sources: venting tanks back to the gas mains; blanketing with coke oven gas. The potential for application of venting and coke oven gas blanketing should be determined by further study. Alternative technologies for dephenolization, cyanide handling, and desulfurization should be further studied with respect to their relative environmental impacts. Solid wastes present hazards in disposal that require further investigation. Wastewater treatment capabilities and effects need further delineation. Economic models of the annualized costs of alternative processes should be further developed to permit delineation of most cost effective technologies.

2.0 CONCLUSIONS AND RECOMMENDATIONS

As this study was a Level 1 assessment, the conclusions offered are all of a preliminary nature, based on grab samples of single sources at one plant. Several areas of potential concern were identified, however, as enumerated below:

1. Emissions from the final cooler cooling tower exceeded the MATE values for hydrogen cyanide and benzene and the emissions rate was 3,200 sm^3/Mg coke.
2. Emissions from the various hydrocarbon storage tanks in the by-product plant exceeded the MATE values for benzene in all cases sampled, although the emissions rate was low in comparison to the final cooler cooling tower.
3. Naphthalene is qualitatively the PNA emitted in the greatest quantity from by-product plant sources, although it was not quantified. The quantity of high boiling PNA's emitted from sampled sources was around 16 g/Mg coke, assuming all organics adsorbed on the resin with boiling points above 300°C to be PNA's.
4. Four hour integrated samples upwind and downwind of the by-product plant did not detect a significant change in benzene or light hydrocarbon concentration across the plant. The average of two 24-hour integrated upwind-downwind samples for hydrogen cyanide detected an increase across the plant from 0.006 vppm to 0.06 vppm (MATE value for HCN is 10 vppm).
5. Organic analysis of the biological plant sludge indicated that several compound classes exceeded the lowest MATE value for that class.

The recommendations offered as a result of this study are basically a call for more detailed examination of the sources identified as potential problem areas followed by a search for control technology if problems are confirmed. The technique used in this study to identify problem areas is conservative; detailed study of an emission which showed that an especially toxic pollutant was not actually present in that emission could eliminate it as a source of concern.

The high aromatics--particularly benzene--emissions from storage tanks are not figments of the procedure, and research into control techniques is needed. Several approaches to vapor recovery are common in the petroleum industry; their applicability to this napthalene-rich emission is not known and will probably have to be field tested. A vapor recovery system plugged with naphthalene will be of little value.

Potential vapor emissions from the aeration basins and holding ponds of wastewater treatment systems are not adequately treated in the literature. Work on this potential problem is recommended.

The final cooler cooling tower was found to be the greatest single emission source in the plant. Resolving this problem will require careful and detailed study, as the emissions from the final cooler cooling tower are linked to effluent quality, at least with respect to cyanide. Cyanide must be removed from the coke oven gas, especially if it is to be desulfurized, but no highly specific, inexpensive cyanide removal process is available.

Turning to sampling and analysis procedures, three problems with the Level 1 protocol became apparent as this study progressed:

1. Sources with very high organic concentrations cause sampling problems (plugging and resin overloading) and analysis problems (bleed through between GRAV and TCO and in the LC cuts). A modified procedure for high concentration sampling should be developed.
2. The analysis is fairly extensive on the GRAV mass, but inadequate with respect to TCO. This is important for samples with more TCO than GRAV.
3. Solvent interference for the heated inlet LRMS runs degraded severely the value of the LRMS, and without the LRMS, analysis of the IR is very difficult.

3.0 INTRODUCTION

The by-product coking industry in the United States is large--about 60 plants--and well-established. The plants often date back to the 1920's or earlier, and were designed and built with the object of profitably recovering by-product chemicals. As might be expected, the industry is diverse, with two or more proven ways to do most of the processing operations. Plants built more recently show the impact of changing chemical markets, as none of the coal chemicals are now profitable to recover. The shift has been toward using the by-product plant to clean coke oven gas for fuel, recovering those materials that can be used, and economically disposing of the rest. Today, with the increase in petroleum prices, the new posture for by-product plants has not fully developed.

The preponderance of older facilities in the by-product industry means that pollution control as mandated today was not built in. The pollution control facilities have been added to existing plants piecemeal, and no single approach has surfaced as a best choice. Most of the past study of by-product coking was directed at its potential as an industrial process, not its effect on the environment. What has been done generally emphasized a particular pollutant or medium, and did not give polynuclear aromatic compounds (PNA's) the attention we now think they deserve.

This study is intended to evaluate the environmental impact of by-product coking by utilizing available information and by developing additional data where required. Screening type (Level 1) sampling and analysis procedures have been used on what are thought to be the most significant potential sources. The results of all the work are presented in this report to provide an overview of the environmental effects of the by-product coking industry.

4.0 PROCESS DESCRIPTIONS: COKE BY-PRODUCT RECOVERY PLANTS

4.1 OVERVIEW OF COMPONENTS AND PROCESSES

Many processes have been developed over the past 100 years or so which transform coal into a variety of useful products. This discussion is limited to the high temperature (around 1000°C) carbonization of "coking" coals with the primary object of producing metallurgical coke. The purpose of the by-product recovery plant is to separate and concentrate the volatile compounds produced and vented from the coke ovens. This report deals with the common industrial practices for recoverying by-products. The initial subject of this introductory discussion is the composition of the raw gas leaving the coke oven, followed by an overview of the process. The major processing options are discussed more fully in succeeding sections.

Components

The operation of a coke oven is cyclic over a 16-20 hour period, and the gas composition and rate from a given oven changes as the coking operation progresses. As 50-60 ovens are often built into a single coke battery, the overall gas rate and composition are nearly constant in the short term. An overall look at the major gas components from coke plants in the United States in 1975 is given in Table 4.[1] The fraction of the coal accounted for specifically in Table 4 is 94.6 percent; the balance is mostly the water driven off or formed during coking.

Coke Breeze--

Coke breeze as identified in Table 4 is simply the fines (roughly less than 2 cm) which are separated from the coke at the coke screening stations. "Breeze" is not part of the feed to a by-product recovery plant.

Coal Tar--

Coal tar is a complex mixture of organic compounds most of which condense in the gas mains leading from the battery to the recovery plant. This

TABLE 4. COKING PRODUCTION STATISTICS-BY-PRODUCT COKE PLANTS, 1975[1]

Coal Carbonized (coked)	74,804,000 Mg	(82,284,000 tons)
Average volatile content	30.7 %	
Average sulfur content	0.9 %	
Range of sulfur contents	0.7-1.2 %	
Coke Produced	51,242,000 Mg	(62,003,000 tons)
Coke yield, based on coal	68.5 %	
Range	62.3-72.8 %	
Coke Breeze Recovered	3,883,000 Mg	(4,271,000 tons)
Average yield, based on coal	5.2 %	
Range	2.8-8.1 %	
Crude Tar Produced[a]	2,860,000 Mg	(3,146,000 tons)
Average yield, based on coal	3.8 %	(7.8 gal/ton coal)
Range	2.9-4.7 %	
Sulfate equivalent of all ammonia products[b] (NH_3 content is 25.8%)	598,000 Mg	(658,000 tons) (4.1 lb NH_3/ton coal)
Average yield, based on coal	0.8 %	
Range	0.7-0.9 %	
Crude Light Oil[c]	634,000 Mg	(697,000 tons)
Average yield, based on coal	0.9 %	(2.4 gal/ton coal)
Range	0.6-1.1 %	
Coke Oven Gas Produced[d]	11,967,000 Mg	(13,164,000 tons)
Average yield, based on coal	16.0 %	(10,860 ft^3/ton coal)
Range	14.3-20.3 %	

[a] Based on an average density of 1.17 g/ml (Rhodes[2]).

[b] Ammonia yields may be understated due to problems in reporting procedures.

[c] Based on an average density of 0.86 g/ml (Glowacki[3] and hydrocarbon densities).

[d] Based on gas density of 0.472 g/l; calculated from composition by McGannon[4].

is by no means a rigorous definition, and various high boiling organic streams throughout a by-product plant may be combined with the coal tar. In appearance tar is a heavy oil, fluid at ambient temperature and with a specific gravity of about 1.2. The composition varies considerably from plant to plant, as would be expected. Table 5 gives the average amounts of some important components of American coal tars.

Ammonia--

Ammonia is reported in Table 4 as the sulfate equivalent because most coke oven ammonia is ultimately recovered and sold as ammonium sulfate. Other forms of by-product ammonia made in the U.S. include anhydrous ammonia and diammonium phosphate.

Light Oil--

Light oil is a clear yellow-brown oil with a specific gravity of around 0.86. It is the coal gas components with boiling points between roughly 0 and 200°C. Over a hundred components have been identified, with benzene being the primary constituent at 60 to 85 percent. Other major components are toluene (6 to 17 percent), xylenes (1 to 7 percent), and solvent naphtha (0.5 to 3 percent). Table 6 presents a representative list of compounds in light oil and some composition data.

Coke-Oven Gas--

Coke-oven gas is the gas which does not condense during the by-products processing. A representative analysis has been presented by McGannon,[4] and is included here as Table 7. The heating value of coke oven gas is generally around 20 MJ/m^3 (500-600 Btu/scf).

The components discussed above are the major components of a coke oven gas after by-product removal without desulfurization; many minor compounds are also present. Consideration of these is not straightforward, as data are scarce and wide variations exist. Compounds such as H_2S, CO_2, HCN, and HCl are frequently removed to some extent in processing the gas.

Sulfur Compounds--

The estimation of H_2S concentrations might seem to be straightforward, but it is not because an uncertain fraction of the sulfur originally

TABLE 5. AVERAGE AMOUNTS OF IMPORTANT COMPONENTS, COKE OVEN TARS [5]

Components		Wt. % of Dry Tar
Benzene		0.12
Toluene		0.25
α-Xylene		0.04
m-Xylene		0.07
p-Xylene		0.03
Ethyl benzene		0.02
Styrene		0.02
Phenol		0.61
o-Cresol		0.25
m-Cresol		0.45
p-Cresol		0.27
Xylenols		0.36
High boiling tar acids		0.83
Naphtha		0.97
Naphthalene		8.80
α-Methyl naphthalene		0.68
β-Methyl naphthalene		1.23
Acenaphthene		1.06
Fluorene		0.84
Diphenylene oxide		---
Anthracene		0.75
Phenanthrene		2.66
Carbazole		0.60
Tar bases		2.08
Medium-soft pitch		63.5
	SUBTOTAL	86.46%
	NOT SPECIFIED	13.54%

TABLE 6. REPRESENTATIVE COMPOUNDS IN COKE OVEN LIGHT OIL AND AVERAGE COMPOSITIONS[6]

Compound	Concentration by Volume %	Compound	Concentration by Volume %
AROMATICS		SULFUR COMPOUNDS	
Benzene	56.5	Hydrogen Sulfide	—
Toluene	16.5	Carbonyl Sulfide	—
Xylenes	5.2	Carbon Disulfide	0.3
Ethylbenzene	0.5	Thiophene	0.2
Naphthalene	1.0	Mercaptans	—
Other C_9 & C_{10} Aromatics	—	NITROGEN COMPOUNDS	
PARAFFINS		Hydrogen Cyanide	—
n-Pentane	0.2	Acetonitrile	—
n-Heptane	—	Pyridines	—
n-Octane	—	OXYGEN COMPOUNDS	
n-Nonane	—	Phenols	—
n-Decane	—	Cresols	—
NAPHTHENES		OTHERS	
Cyclopentane	0.2	Wash Oil	4.0
Cyclohexane	0.1	Solvent Oils	1.0
Substituted Cyclohexanes	—	Pitch Residue	
UNSATURATES			
1-Butene	—		
Butadiene	—		
Amylenes	0.4		
Cyclopentadiene	0.7		
1-Hexene	—		
2-Hexene	—		
Hexadiene	—		
Cyclohexene	3.0		
1-Heptene	—		
Styrene	0.8		
Indene			
Coumarone	3.0		
Others			

TABLE 7. REPRESENTATIVE COKE OVEN GAS

Component		Volume %
CO_2		1.4
H_2S		0.6
O_2		0.4
N_2		4.3
CO		5.6
H_2		55.4
CH_4		28.4
C_2H_4		2.5
C_2H_6		0.8
Illuminants*		0.6
	TOTAL	100.0

*Treated as propylene

present in the coal is retained in the coke. A statistical analysis of the Bureau of Mines-AGA tests revealed a good correlation which would give 60 percent of the sulfur going to the coke.[7] Table 8 presents a selection of these data from a more recent publication of results from this continuing effort.[8] The seven counties shown together supplied close to half of the coal carbonized in 1975. Furthermore, although most of the sulfur volatilized is found as H_2S, that component splits between the raw gas and the weak ammonia liquor in a complex fashion. We will assume that, of the nine units of sulfur in 1000 units of air-dried coal, six emerge with the coke and three with the products. Arbitrarily, let two of these three go with the raw gas, one temporarily with the weak liquor.

Not all the sulfur in the raw gas is present as H_2S. The compounds CS_2, COS, CH_3SH and still others can be identified. Since CS_2 is the principal sulfurous contaminant other than H_2S, it will be loosely quantified. At a rate of 1 to 2 percent of the sulfur in the coal,[9] the amount in the raw

TABLE 8. SULFUR AND NITROGEN IN COAL AND COKE[8]

Source[a]	S in Coal	Nitrogen in coal	Coke Yield	S in Coke[c]	Nitrogen in Coke[c]
Jefferson Co., AL	0.7-0.9	1.4-1.6	69.8-75.6	0.7-0.8	1.1-1.5
Pike Co., KY[e]	0.5-1.4	1.3-1.7	63.3-77.8	0.5-0.7	1.1-1.6
Cambria Co., PA	0.8-2.3	1.2-1.4	64.8-90.1	0.7-1.7	1.1-1.5
Greene Co., PA		1.5-1.6	68.0-70.2		
Washington Co., PA[d]	1.0-1.3	1.2-1.6	63.7-72.5	0.9-1.4	1.0-1.6
Logan Co., WV[f]	0.5-0.8	1.3-1.8	65.5-79.3	0.5-0.7	1.0-1.8
McDowell Co., WV	0.5-1.4	1.1-1.6	63.4-90.8	0.6-0.8	0.6[b]-1.2

[a] Counties supplying more than 4 million short tons, 1975.[1]

[b] This result and another at 0.9 are exceptional.

[c] Omitting analyses of blends, components of which are usually from other mines, counties, or even states.

[d] Excluding Terminal No. 9, Westland, and Twilight mines, all high sulfur coals.

[e] Excluding Borderland mine, a high-sulfur coal.

[f] Excluding Big Creek, Winisle No. 1, Elk Creek No. 3, Paragon, Cedar Grove No. 7, and Upper Cedar Grove No. 15 mines, all high sulfur coals.

coal gas is on the outside about 0.2 units per 1000 units of coal. It is perhaps not out of place here to observe that the ratio of CS_2 to H_2S in coke oven gas, about one in twenty, is conspicuously higher than in petroleum refinery fuel gases. This fact influences the choice among desulfurization processes.

Nitrogen Compounds--

Nitrogen compounds of interest, in addition to ammonia, include hydrogen cyanide and the tar bases. We will first discuss the source of the nitrogen and then the compounds. Table 8 includes data indicating the amount of nitrogen in some coals. The data in Table 8 suggest that the nitrogen originally present divides almost pro rata between the coke and the volatiles, i.e., some 65-75 percent of the nitrogen in the coal is fixed in the coke. (This can be compared with a rule-of-thumb of 50 percent published in 1924.[10]) On this basis gaseous nitrogen should amount to about 0.3 percent of the coal charged. The data in Table 5, converted to weight percent, give a gaseous nitrogen content of 1.8 percent based on the coal. It is probable that much of this unaccounted-for nitrogen is a consequence of air introduced at charging or infiltrating into the negative pressure gas main. The free oxygen in coke oven gas is another indicator of air infiltration.

Ammonia is the most important of the nitrogen compounds, representing about 0.20 percent of the coal carbonized in 1975. The nitrogen content of the ammonia, compared to a representative 1.4 percent nitrogen in the coal suggests that about 12 percent of the coal nitrogen emerges as ammonia. This is somewhat below the classical rule-of-thumb, 18 percent,[10] reflecting the higher coking temperatures and coking rates of modern industrial practice,[11] with consequent decomposition of some primary ammonia.*

Tar bases are also important nitrogenous by-products. The label "tar bases" properly embraces pyridine (C_5H_5N) and its substituted homologs (picolines, lutidines), quinoline (C_9H_7N) and its homologs, acridine ($C_{13}H_9N$), etc. The customary nomenclature can be stretched to include the cyclic secondary amines pyrrole (C_4H_5N) and its homologs, indole (C_8H_7N), carbazole ($C_{12}H_9N$), and even primary amines such as aniline (C_6H_7N) and toluidines (C_7H_9N).

Kirner[12] summarizes Bureau of Mines findings through 1939 by stating that "The quantity of nitrogen bases obtained in the distillation of American coals over the temperature range 500-1100°C does not vary appreciably." Since the coals and the carbonization process have changed little since those findings, we will assume that they still pertain. Kirner goes on to say that the unrefined light oil contains 1-3 percent pyridine and its

---

*It can be shown with the aid of standard thermodynamic data that equilibrium in the dissociation reaction

$$2NH_3 \rightleftarrows N_2 + 3H_2$$

is far to the right at all temperatures of interest. The effect of temperature and the catalytic influence of certain solids, especially iron, on reactions rates is reviewed by Hill.[10] The so-called protective action of steam mentioned by Hill is probably competitive chemisorption on the catalytic surfaces.

lighter homologs, and the tar contains 2.3 percent tar bases and a like amount of carbazoles. Using these rough figures with the gross split of Table 8, the nitrogen bases in the light oil amount to perhaps 0.02 percent of the coal, those in the tar to about 0.2 percent. If these amounts were all pyridine, which is about 18 percent nitrogen, the total of nitrogen bases would account for about 3 percent of the nitrogen in the coal, consistent with an old rule-of-thumb.[10]

Hydrocyanic acid (hydrogen cyanide, loosely called cyanogen in the industry) is important not only because its cyanide ion emerges as a water pollutant but because it interferes with sulfur recovery. The formation of HCN according to the reaction

$$CH_4 + NH_3 \rightleftarrows HCN + 3H_2$$

is thermodynamically favorable above about 800°C. But the reaction is evidently slow in coke ovens. The cyanogen content of a typical American coke oven gas is 1.37 g/m^3 [13] compared to about 7.6 g/m^3 of H_2S for the 0.9 percent sulfur in 1975 coking coal.[14] (Nothing like this much cyanogen is found in the desulfurization of fuel gases in petroleum refineries.) On a weight basis, the cyanogen is 0.003 g per gram of gas, or 0.5 g per kilogram of coal; since cyanogen is about half nitrogen, this means that about 2 percent of the coal nitrogen emerges as HCN, as has been traditionally observed.[10]

Chlorine Compounds--

Chlorine in coal is so little a problem in this country that it is not reported in so-called "ultimate" analyses.[15] Moreover, it occurs primarily as the water-soluble minerals halite (NaCl) and sylvine (KCl), and is largely removed in the wet processes by which most coking coals are cleaned.[4] What remains is usually assumed to distill during carbonization, primarily as HCl.

Oxygen Compounds--

As has been noted, there is some oxygen in coke oven gas which is unlikely to have come from the coal. That in the coal is found primarily as CO_2, CO, and H_2O. The important oxygen compounds for present purposes, however, are the "tar acids": phenol (C_6H_6O) and its homologs, naphthols ($C_{10}H_8O$) and their homologs, catechols ($C_6H_6O_2$), etc. These are toxic to biota in receiving waters and, when chlorinated during water treatment, even a few parts per billion impart an unacceptable taste to drinking water.[16]

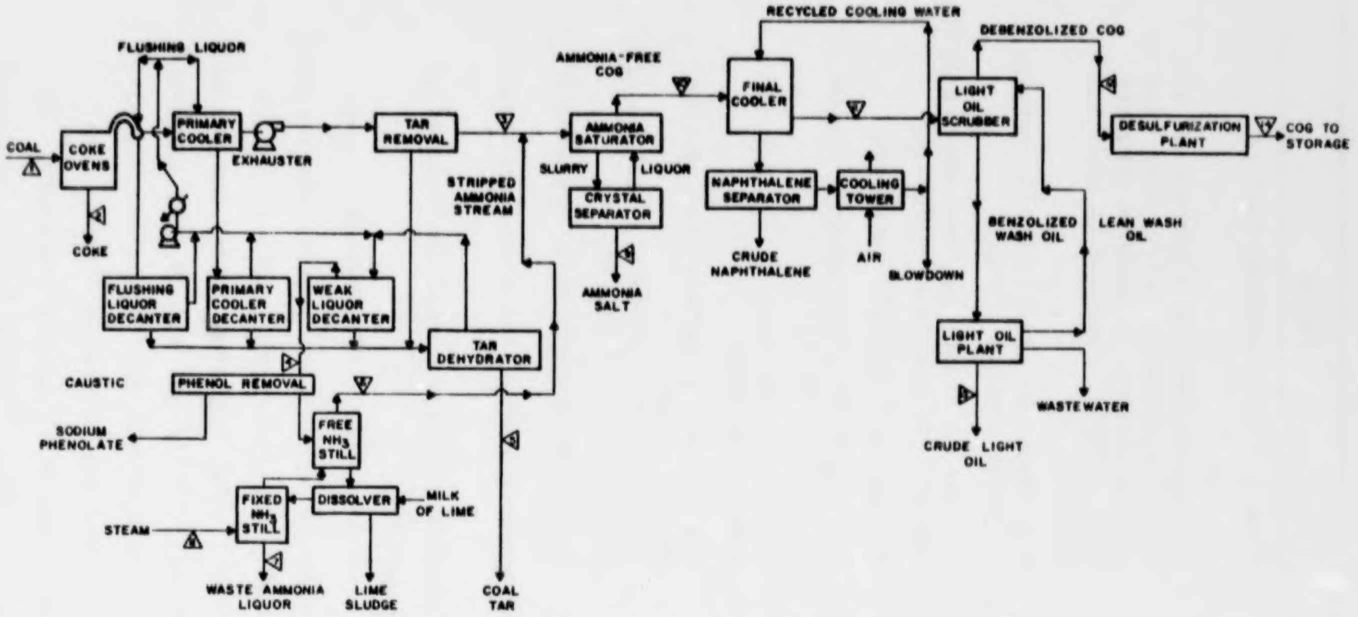
Coal with the national average volatile content, 30 percent, carbonized at 900-1000°C as is typical in this country, should give a tar containing 2-3 percent tar acids.[17] Thus 1000 units of coal produce 38 units of tar containing 1 unit of tar acids.

Process Overview

This process description section describes the mainstream of U.S. coke by-product recovery operations. An overview is presented below, and more complete descriptions in the following sections. There are generally two or three ways, more or less widely used, to do any of the recovery operations. Section 5 of this report discusses the prevalence of the various processes in the United States.

The flowplan and material balance of a representative coke by-product recovery plant is given as Figure 1. More detailed information is included in later sections. Table 9 summarizes the fate of the major coke oven by-products in a representative plant.

The gases leaving a coke oven are generally at around 700°C and of course contain all of the material to be processed in the by-product plant. Coke ovens are maintained at a slight positive pressure (1 mm water) to prevent air infiltration. As the gas leaves the oven it is subjected to spray cooling immediately, both to cool the gas and to introduce a collecting medium for the tar as it condenses. After a short duct run the gas passes through a valve and enters a suction main, remaining below atmospheric pressure. At this point, the gas has generally been cooled to the 100°C range; much of the water, tar, and ammonia, along with other compounds, have been condensed. Further removal by condensation is accomplished in the primary cooler and tar removal process steps. The tar and the water soluble compounds are separated by decantation. The tar is generally further dewatered before sale. If phenol is recovered from the ammonia liquor, it is often absorbed in an organic solvent before the ammonia recovery step. The ammonia liquor is traditionally steam-stripped to put the ammonia back into


COAL
COKE OVENS
COKE
FLUSHING LIQUOR
PRIMARY COOLER
EXHAUSTER
TAR REMOVAL
FLUSHING LIQUOR DECANTER
PRIMARY COOLER DECANTER
WEAK LIQUOR DECANTER
TAR DEHYDRATOR
CAUSTIC
PHENOL REMOVAL
SODIUM PHENOLATE
FREE NH_3 STILL
FIXED NH_3 STILL
DISSOLVER
MILK OF LIME
STEAM
WASTE AMMONIA LIQUOR
LIME SLUDGE
COAL TAR
STRIPPED AMMONIA STREAM
AMMONIA-FREE COG
AMMONIA SATURATOR
SLURRY
LIQUOR
CRYSTAL SEPARATOR
AMMONIA SALT
RECYCLED COOLING WATER
FINAL COOLER
NAPHTHALENE SEPARATOR
CRUDE NAPHTHALENE
COOLING TOWER
AIR
BLOWDOWN
DEBENZOLIZED COG
LIGHT OIL SCRUBBER
BENZOLIZED WASH OIL
LEAN WASH OIL
LIGHT OIL PLANT
WASTEWATER
CRUDE LIGHT OIL
DESULFURIZATION PLANT
COG TO STORAGE
1
2
3
4
5
6
7
8
9
10
11
12
13
14

KG/DAY	1 COAL	2 COKE	3 RAW GAS	4 NH LIQUOR	5 TAR	6 STRIP	7 WASTE LIQUOR	8 STEAM	9 SALT	10 COG	11 COG	12 COG	13 CRUDE LO	14 COG
CARBON SOLIDS	10,000[a]	7370												
WATER	500		100	900	8	110	1040	250		240	140	130		130
CARBON DIOXIDE			89	1		1				90	90	85		80
HYDROGEN SULFIDE			29	1		1				30	30	30		2
AMMONIA NITROGEN			15	5		5			20					
CYANIDE			4	1		1	TRACE			5	3	3		
CHLORIDE				1			1							
GASES: H_2, CO, CH_4, N_2, O_2, HC			1500							1500	1500	1500		1500
CARBON DISULFIDE			2							2	2		2	
LIGHT OILS			90		8					90	90	5	85	5
TAR ACIDS				1	10		TRACE							
TAR BASES			2		10					2	2		2	
POLYCYCLICS			1		340					1				
OTHER							Ca: 1		SO_4: 53					
TOTALS	10,500	7370	1840	910	380	120	1040	250	73	1960	1860	1760	90	1720
TEMPERATURE °C			60	30	30	95	105	130		45	30	30		30
PRESSURE, bars			1.1			1.1		2.7		1.05	1.04	1.02		1.0

a. BASIS: THE SCALE FACTOR TO DUNLOP AND McMICHAEL (36) IS 550
b. ROUNDED

Figure 1. Flowplan and material balance of a representative coke by-product recovery plant.

TABLE 9. FATE OF COKE OVEN BY-PRODUCTS

Component	Route
H_2, CH_4, and light hydrocarbons, N_2, O_2, CO, and CO_2	Remain in gas; used as fuel gas
Ammonia	Via gas to ammonia scrubber, or via liquor to ammonia still, then back to gas and thence to ammonia scrubber. Most ammonia converted to ammonium sulfate.
Water	Via liquor to ammonia still, remains as waste ammonia liquor.
H_2S, HCN	Via gas or liquor to free ammonia still, thence into gas to desulfurizer
Benzene, Toluene, Xylene	Via gas to light oil scrubbers
HCl	Via liquor to waste ammonia liquor as $CaCl_2$ (lime still)
Tar bases (C_5H_5N, etc.)	Condensed into tar, or via gas to ammonia scrubber.
Tar acids (phenol etc.)	Via liquor to dephenolizor, or condensed as tar.
Naphthalenes	Condensed in tar, or via gas and condensed in final cooler.
Heavy organics (boiling point >200°C)	Condensed as tar (small fraction to light oil).

the gas stream, as shown. The waste ammonia liquor requires addition of a base to release some chemically bound ammonia.

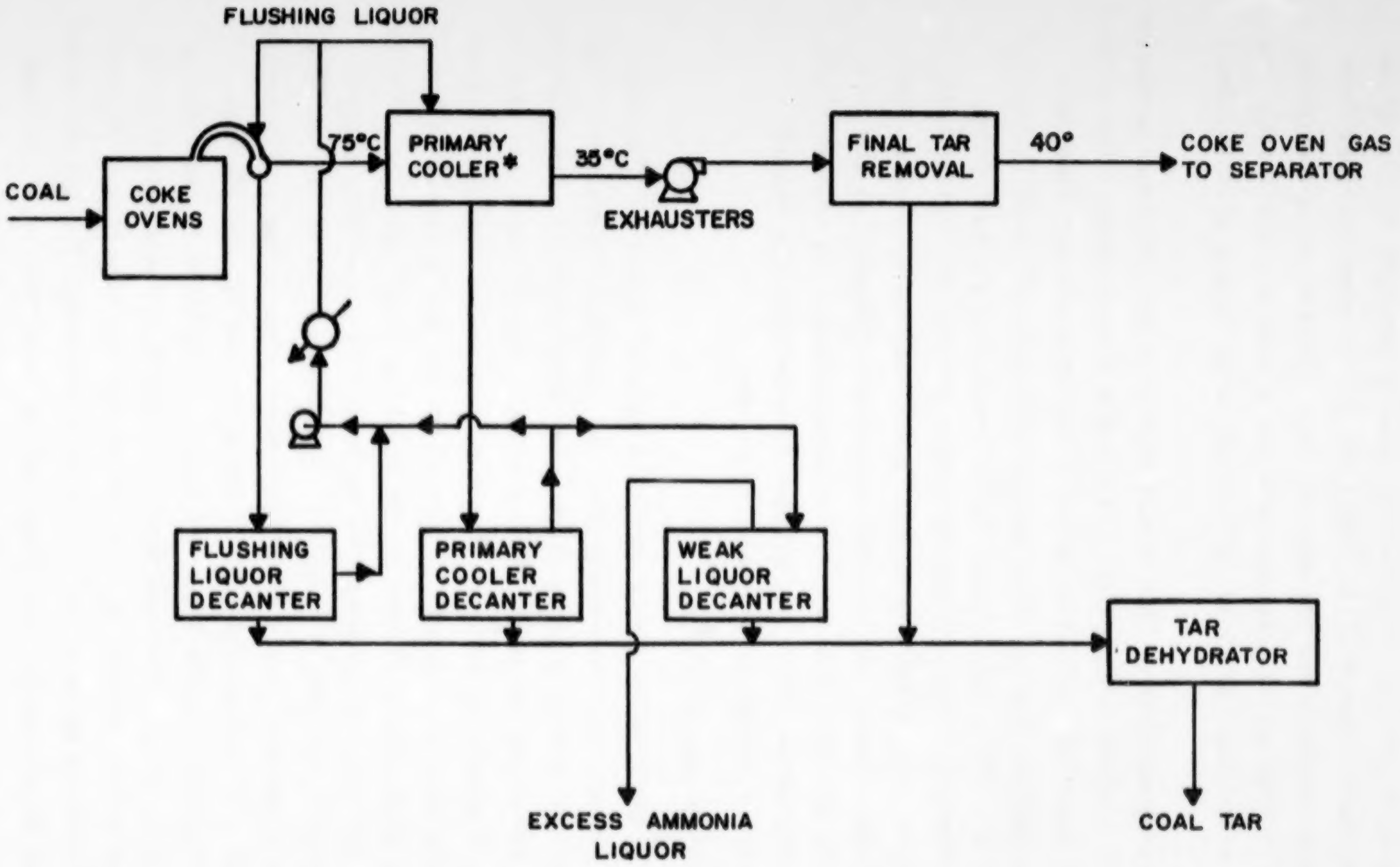
Looking again at the gas stream, the exhauster is the fan which provides motive power for the gas. Tar removal effects nearly complete recovery of the tar remaining in the gas, generally as particulate; both scrubbers and electrostatic precipitators are used in the industry. After the ammonia stripped from the waste ammonia liquor rejoins the gas stream, the ammonia can be scrubbed from the gas with a dilute sulfuric acid solution. Ammonium sulfate crystals form and are separated from the saturated liquor. The final cooler is a pretreatment step for light oil (benzene) recovery. In the process, generally contact cooling with water, naphthalene is condensed from the gas. The naphthalene may be removed from the water by absorption in organics or by flotation. Light oil is usually recovered by absorption in a petroleum fraction (wash oil). The light oil is steam stripped from the wash oil and recovered and the wash oil recirculated. Desulfurization, if practiced, is intended to make coke oven gas a more acceptable fuel. No process is in widespread use today; only a few larger plants practice desulfurization.

The following sections of this report deal with the individual processes in more detail. Further information is available from sources listed in the references. A good first selection would be the coke and coal chemicals chapter of The Making, Shaping, and Treating of Steel, published by the U.S. Steel Corporation. The reader should remain aware that at least three powerful influences militate against any single process description being widely applicable: (1) today's by-product plants have often evolved over 20-50 years of maintenance, design, and operational changes, (2) the technology is mature and there are many proven alternate ways to recover chemicals, and (3) the market for coal chemicals is uncertain, and economic pressure has led to changes in operating philosophy.

4.2 TAR SEPARATION AND PROCESSING

Coal tar is produced in a coke oven at a rate of around 30 l/Mg coke (8 gal/ton). Figure 2 outlines the primary tar separation operations. The condensation of tar initially takes place under direct contact with flushing liquor in the collecting mains and suction mains. The gas mains are sprayed and vigorously flushed with recycled liquor both to quench the gas and avoid buildup of tarry deposits. Around 70 percent of the tar is separated from the gas in the mains and is flushed to the flushing liquor decanter. Another 20 percent of the total is condensed and collected in the primary cooler, along with a significant amount of water. Tar continues to be removed from the gas in the exhausters, and a final tar removal step (often precipitators, sometimes scrubbers) removes the last of the entrained tar particulate.

Each of these tar/ammonia liquor streams is traditionally separated by gravity, generally in more than one separation device. These decanters are commonly vented to the atmosphere; they may or may not have tops. The level of separation achieved by decantation is highly variable. Typical residence times are about 10 minutes for the liquor and 40 hours for tar.[19] A common


FLUSHING LIQUOR
COAL
COKE OVENS
75°C
PRIMARY COOLER*
35°C
EXHAUSTERS
FINAL TAR REMOVAL
40°
COKE OVEN GAS TO SEPARATOR
FLUSHING LIQUOR DECANTER
PRIMARY COOLER DECANTER
WEAK LIQUOR DECANTER
TAR DEHYDRATOR
EXCESS AMMONIA LIQUOR
COAL TAR

*This flowplan includes a direct contact primary cooler. Indirect primary coolers utilizing noncontact cooling water are also fairly common.

Figure 2. Tar separation.

target for water in coal tar is around 2 percent;[6] multiple decanting stages may be used with final dewatering by centrifugal separator or heating in storage. Chemical emulsion breakers are sometimes used.

Processing

Coal tar can be refined to produce a number of chemicals. Considine[20] has outlined a complete process route for coal tar, which is presented in Figure 3. The precise state of tar refining in the United States is somewhat uncertain today. The coke/coal tar industry was once the exclusive source of such chemicals as naphthalene, pyridine, phenol, and their derivatives. Competition from petroleum based chemicals has made serious inroads into the coal chemicals market. Bureau of Mines reports,[21] confirmed by annual AISI directories,[22] indicate that only a few (4-8*) coke producers practice on-site tar refining. The refining that is done on-site need not include all the separations shown in Figure 3. Each tar refining plant was built and operated to meet specific market conditions, and the plant may respond to changing conditions by abandoning a process step (as CF&I did), rearranging the process to add an extra step, or pressing old hardware into new kinds of service. Local markets occasionally allow profitable operation for independent tar distillers who collect tar from several producers. In today's market, it is unlikely that coal tar would be refined at the site of a new coke battery. Some existing equipment has been shut down at various by-product plants. The value of coal tar as a fuel has risen considerably, and smaller producers often burn this tar. Storage of tar is generally in vented, cylindrical tanks at above ambient temperature (perhaps 50-80°C), to permit easy transfer.

4.3 AMMONIA HANDLING

The ammonia produced in a coke oven amounts to around 0.2 weight percent of the coal fed to the ovens. Flushing liquor sprayed into the collecting mains to cool the gas absorbs some of the ammonia, and more is absorbed in the water condensed in the primary cooler (Figure 1). Flushing liquor con-

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*The data on number of producers have been concealed by USBM to avoid disclosing company data.[1]

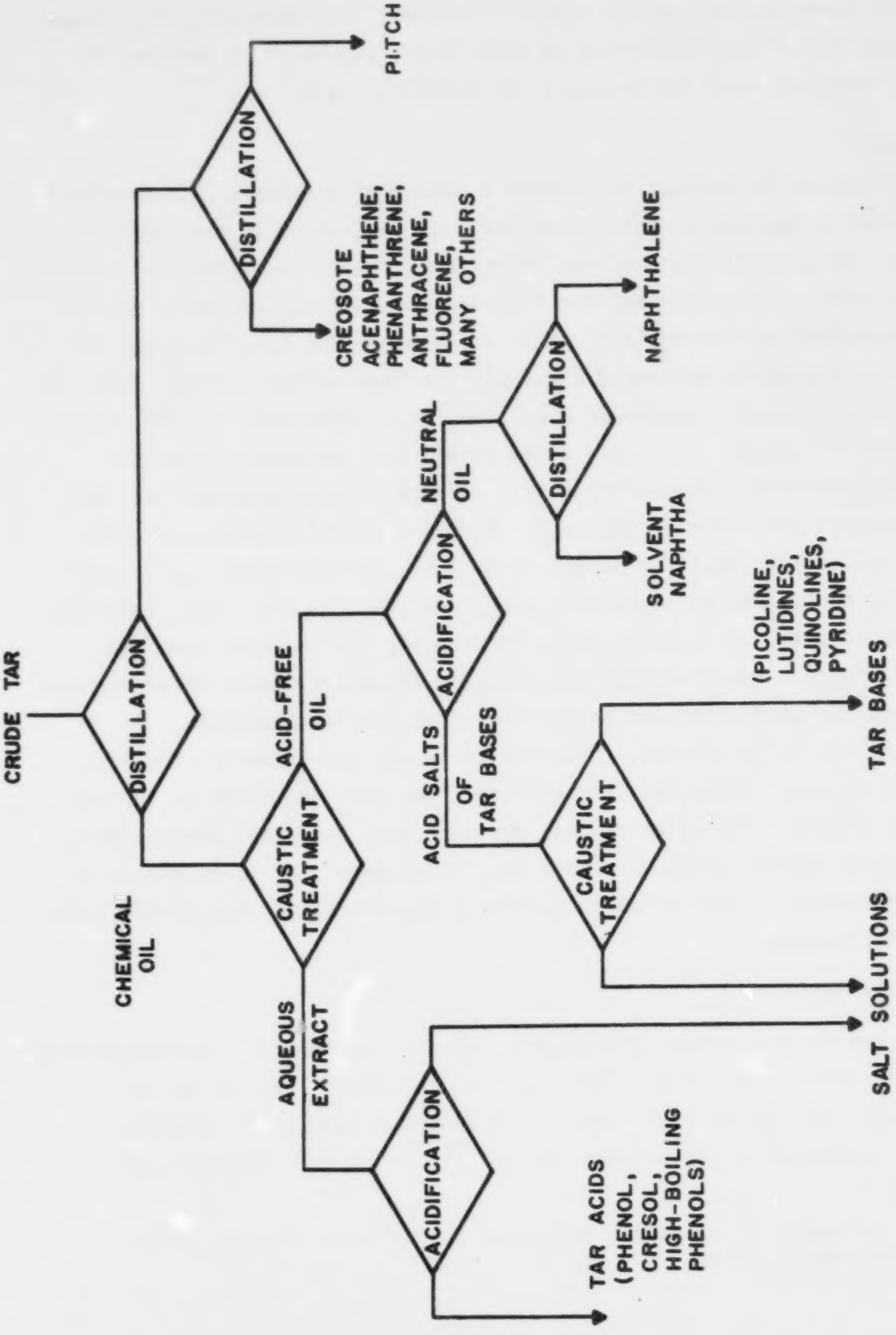

CRUDE TAR
DISTILLATION
CHEMICAL OIL
DISTILLATION
PITCH
CREOSOTE
ACENAPHTHENE,
PHENANTHRENE,
ANTHRACENE,
FLUORENE,
MANY OTHERS
CAUSTIC TREATMENT
ACID-FREE OIL
AQUEOUS EXTRACT
ACIDIFICATION
NEUTRAL OIL
DISTILLATION
NAPHTHALENE
SOLVENT NAPHTHA
ACID SALTS OF TAR BASES
CAUSTIC TREATMENT
TAR BASES
(PICOLINE,
LUTIDINES,
QUINOLINES,
PYRIDINE)
SALT SOLUTIONS
ACIDIFICATION
SALT SOLUTIONS
TAR ACIDS
(PHENOL,
CRESOL,
HIGH-BOILING
PHENOLS)

Figure 3. Tar refining outline.[20]

tains around 5-6 g NH_3 per liter. Along with ammonia, compounds such as hdyrogen sulfide, phenolic compounds (tar acids), and cyanides dissolve in the flushing liquor. The distribution of ammonia between the gas and liquid phases depends on operating conditions and the coal composition. Figure 1 uses a representative split with 75 percent of the ammonia remaining in the gas phase.

Ammonia handling then is a problem of removing the ammonia from both the gas and ammonia liquor streams and achieving satisfactory disposal of any waste. Whatever the scheme for removing ammonia from the coke oven gas, there will always be an aqueous waste because the carbonization of coal produces water.

Several processing options have been developed to recover the ammonia. The cyanide and phenol generated in the coking process must also be dealt with, and are discussed in separate sections of this report. The ammonia handling route shown in Figure 1 is known as the "semi-direct" process, and is the option most common in the United States. All of the ammonia is eventually recovered from the gas stream, but a portion enters the flushing liquor first and is later stripped out. (The "direct" process involves controlling the quenching in the gas mains such that no aqueous waste is condensed. The gas phase, containing practically all the ammonia, is then scrubbed with sulfuric acid to recover the ammonia. This process has many drawbacks and is not practiced in the United States.[6] The indirect process option requires additional water scrubbing to get essentially all the ammonia into the liquid phase, where it is concentrated by distillation. A very few American producers follow this route, producing only aqueous ammonia.[21]) The remainder of this discussion of ammonia handling will deal with the semidirect processing route and its requirements.

Ammonia Liquor Treatment

As was discussed under tar separation, aqueous ammonia solutions are decanted from the tar in a variety of processing vessels. Much of this is recycled as flushing liquor; a portion is constantly drawn off as weak (sometimes excess, crude, or waste) ammonia liquor. The ammonia in the weak ammonia liquor (WAL) must be put into the gas phase for recovery via the acid contactor. The traditional removal technique is steam stripping as shown in Figure 4. The ammonia in the weak ammonia liquor can be thought of as being present in two forms: "free" and "fixed". Free ammonia compounds are those which can be dissociated with heat (ammonium carbonates, sulfides, cyanide, etc.). "Fixed" ammonia compounds are those associated with strong acids (ammonium chloride) which must be dissociated by the addition of a strong base (generally lime or sodium hydroxide).

The actual design and operation of ammonia stills is not as straightforward as it might appear based on the discussion above. The chemical complexity of ammonia liquor requires that designers consider several simultaneous ionic equilibria as well as vapor-liquid equilibria for water and volatile solutes. H_2S and NH_3 might be considered the primary solutes, but also present and interacting are dissolved CO_2, HCN, phenol and various homologs, pyridine and its homologs, and chloride ion. Dealing satisfactorily with all these equilibria has only been practical with the advent of computers, and the results will still be no better than the available data. Most existing ammonia stills were necessarily designed in a somewhat empirical way to meet specific goals with respect to ammonia concentrations; the other components pretty well go along for the ride. Along with ammonia, HCN, H_2S, and phenol can be stripped from ammonia liquor by steam. As shown in Figure 4, the ammonia stripping is commonly accomplished in two more or less separate stills. Free ammonia is stripped in the top (free) still by the steam and ammonia vapor rising from the lower still. A basic solution is added near the center of the tower. Any phenol and cyanides which are not stripped out in the free still are chemically bound by the base and are not removed in the fixed still. The steam injected in the bottom of the lower (fixed) still strips out the ammonia released due to reactions by the change in pH.

The conventional approach to pH adjustment has been the addition of dissolved lime (5-10 percent) to the partially stripped liquor in the "lime leg". The liquor, with a pH of around 11 here, is then exposed to the stripping steam in the fixed still. Caustic solutions are coming into favor for pH adjustment in fixed stills because they allow better pH control, reduce total water usage and eliminate scaling and precipitate problems along with some suspended solids in the effluent from the stills. In addition, the efficiency of the stills is better. Caustic is more expensive,

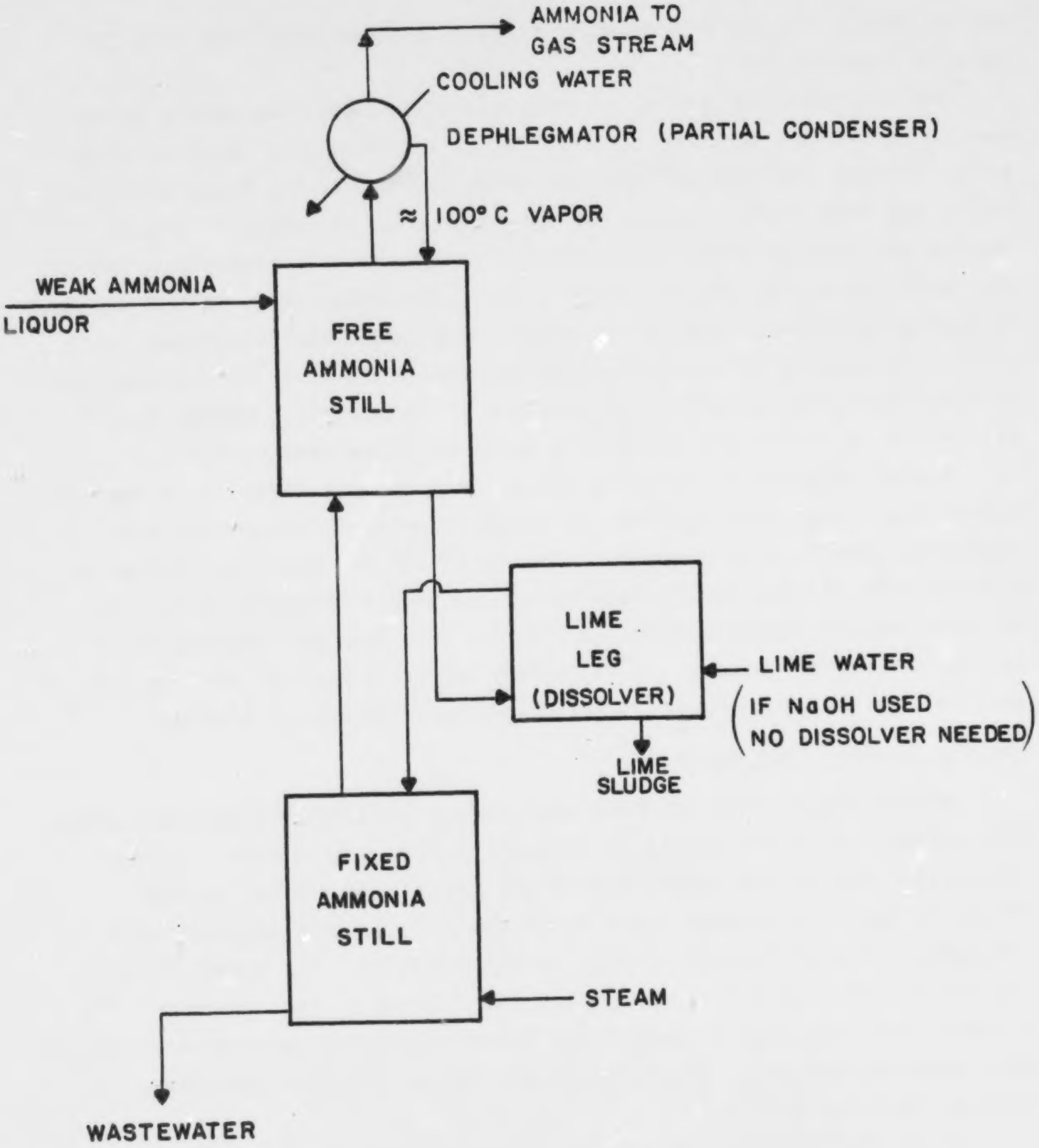

AMMONIA TO GAS STREAM
COOLING WATER
DEPHLEGMATOR (PARTIAL CONDENSER)
≈ 100° C VAPOR
WEAK AMMONIA LIQUOR
FREE AMMONIA STILL
LIME LEG (DISSOLVER)
LIME WATER
(IF NaOH USED NO DISSOLVER NEEDED)
LIME SLUDGE
FIXED AMMONIA STILL
STEAM
WASTEWATER

Figure 4. Ammonia stills.

but apparently the overall operating costs just about break even when compared to lime addition.[23]

The efficiency of removal of ammonia/H_2S/HCN/phenol and others in the ammonia stills is a function of still design and operation. Most existing stills utilize tray-type columns with about 10 trays in the fixed still and 5-6 in the free stills. Bubble-cap trays appear to be common.[4] Liquor leaving the still contains about 0.15 g/l of ammonia. In traditional designs the vapor leaving the ammonia still is partially condensed in a "dephlegmator" to reduce the water content of the vapor. The condensate is refluxed to the still. The ammonia rich vapor leaving the top of the still is then combined with the coke oven gas stream for recovery of the ammonia. Another possibility[24] is to incinerate the ammonia stripped in the ammonia stills.

Another approach to stripping ammonia from ammonia liquor is to use air rather than steam, thus reducing the volume of water in the process and improving overall ammonia removal. The use of air has been investigated on a pilot scale.[23] One disadvantage to the use of air stripping is that the stripped ammonia cannot be combined with the coke oven gas (because air is in the stream) for recovery via the normal route. A separate ammonia processing step (sulfate or equivalent) or incineration must be provided.

Ammonia Recovery from the Gas

Ammonia removal from the coke oven gas has traditionally been by contact with sulfuric acid and recovery of crystalline ammonium sulfate. In the classical (roughtly pre-1930[4]) form of the saturator[13] the raw gas was forced to bubble up through a pool of dilute sulfuric acid saturated with $(NH_4)_2SO_4$. Crystallization occurred in the saturator. The burden of forcing the gas and liquid into contact was thus imposed on the exhauster. The crystals were separated by gravity and the acid solution recycled with make-up acid added as required. The crystals were further dried by centrifuge, washed, and dried again.

In the Otto System,[4] the acid is lifted and sprayed into the top of a short column through which the gas is rising. Better contact (interfacial area per unit of saturator volume) is achieved for less energy. The crystallizer is a separate vessel, but the absorber and crystallizer still interact.

The Wilputte System[4] (Figure 5) divorces the two, achieving better control of crystal size. Here the spray is not saturated with salt and the separate crystallizer is operated by evaporative cooling under sub-atmospheric pressure. Water vapor with entrained impurities passes to two or three steam-jet ejectors in cascade. Barometric condensers exhaust the hot condensate to a sump. The condensate is of a quality which permits the operation of a cooling tower to serve the condensers, but the blowdown is a necessary process discharge.

The ammonium sulfate produced in the semi-direct process has found a progressively poorer reception in the fertilizer market as anhydrous ammonia has gained in popularity. Its marketability was further depressed by rapid growth in the production of caprolactam, a nylon intermediate, which also has ammonium sulfate as a by-product. One possible remedy has been to substitute phosphoric acid for sulfuric; the hardware is the same and operating conditions only slightly different. The by-product is the more marketable di-ammonium phosphate, containing two important plant nutrients instead of one, but at a higher price for the acid. Only two producers chose this route in 1973.[21]

Another remedy, growing out of the foregoing, is the absorption of ammonia in circulating aqueous $(NH_4)H_2PO_4$,[25] the stripping of ammonia from this medium, and the condensation of the concentrated ammonia (Figure 6). Distillation of the product, either with refrigeration or under pressure, yields a substantially pure ammonia which is more readily marketable than are the salts. It appears that the entire coke by-product ammonia output of U.S. Steel's Clairton Works, the largest coke plant in the world, is in the anhydrous form produced by this technology.

Still another remedy to the ammonia disposal problem is the incineration of the ammonia stripped from the scrubbing medium.[26] Noting that the commercial production of nitric acid starts the same way, we can be sure that this thermal destruction of NH_3 must be carefully managed to minimize NO_x production. Low temperatures, low excess air, and slow cooling are recommended. This technology is being practiced by Inland Steel at East Chicago.

4.4 TAR ACID (PHENOL) REMOVAL/RECOVERY

Phenol is one of the minor constituents of coke oven gas, highly vari-

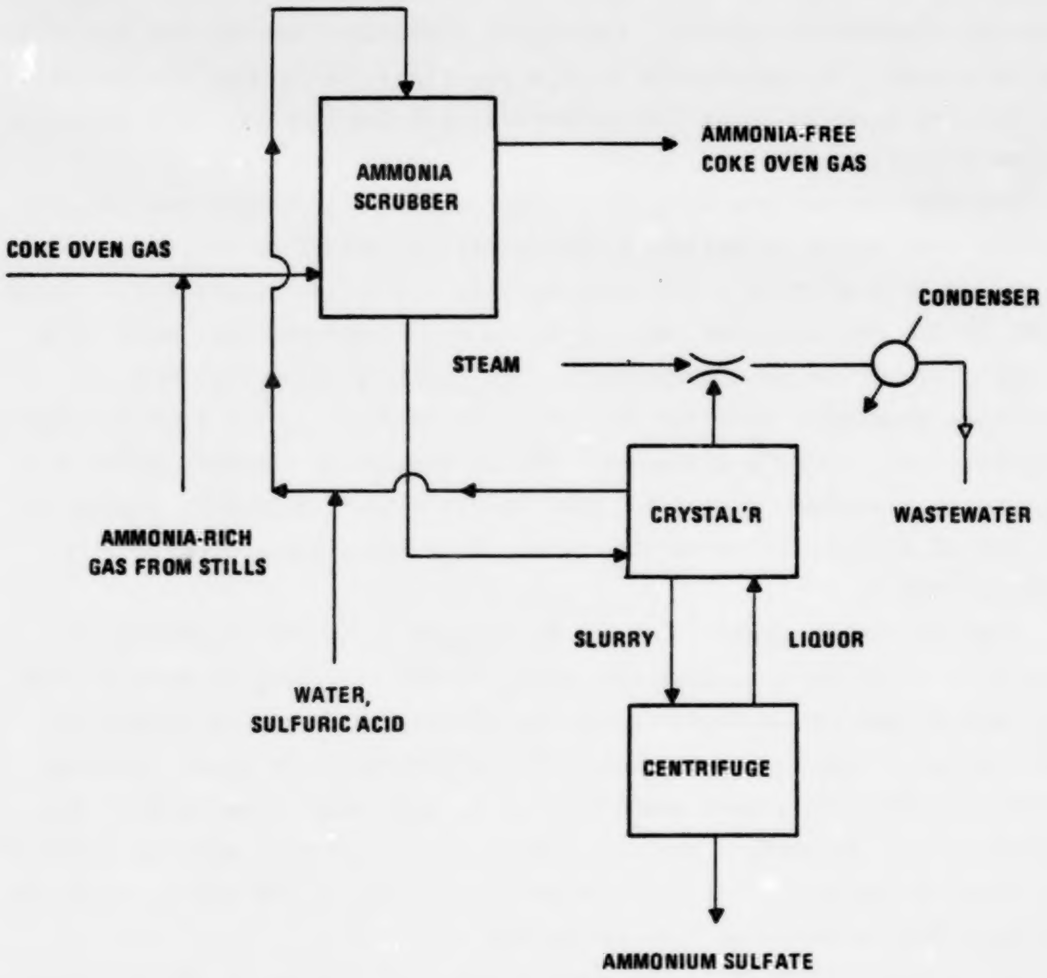

AMMONIA SCRUBBER
AMMONIA-FREE COKE OVEN GAS
COKE OVEN GAS
CONDENSER
STEAM
CRYSTAL'R
WASTEWATER
AMMONIA-RICH GAS FROM STILLS
SLURRY
LIQUOR
WATER, SULFURIC ACID
CENTRIFUGE
AMMONIUM SULFATE

Figure 5. Ammonium sulfate recovery with vacuum crystallizers (Wilputte).

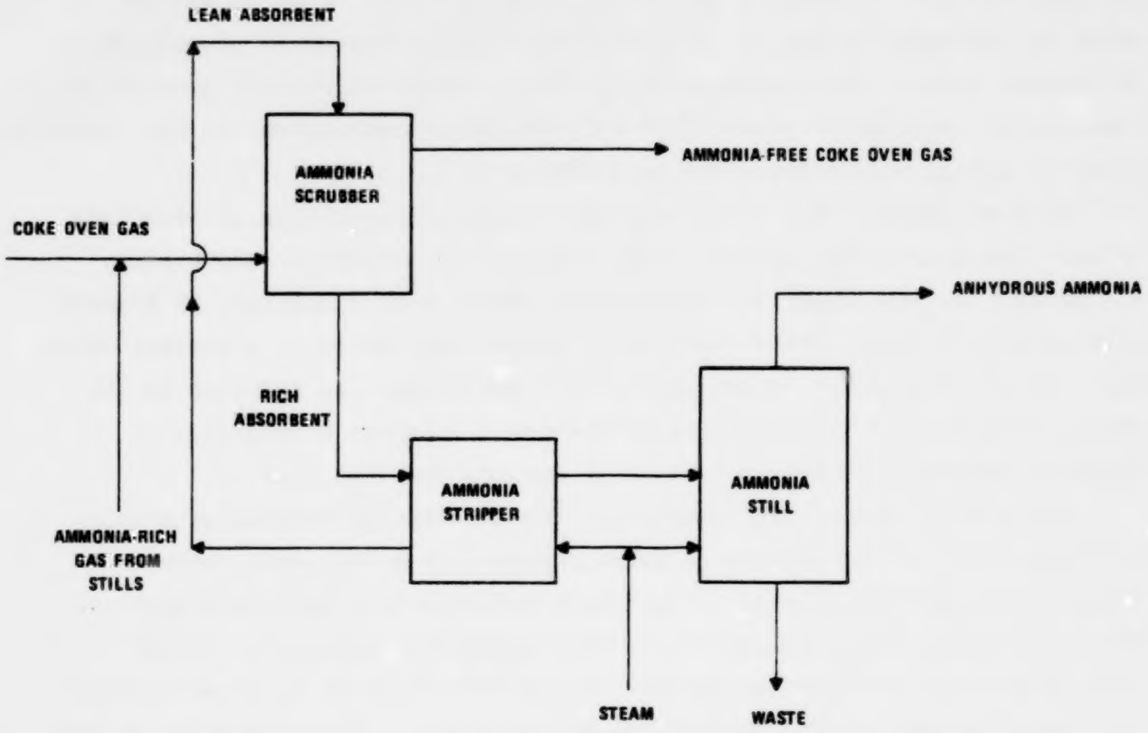

LEAN ABSORBENT
AMMONIA SCRUBBER
AMMONIA-FREE COKE OVEN GAS
COKE OVEN GAS
ANHYDROUS AMMONIA
RICH ABSORBENT
AMMONIA STRIPPER
AMMONIA STILL
AMMONIA-RICH GAS FROM STILLS
STEAM
WASTE

Figure 6. Ammonia recovery by "Phosam" process.[25]

able in concentration as coking practice and coals vary. Most of the phenol in the gas phase is scrubbed into the flushing liquor. One operator has reported phenol concentrations in the excess ammonia liquor between 500 and 4,500 ppm over 20 years of operation and coking times of 13 and 22 hours.[27] The term "phenol" is often used, as was done above, to refer to all the tar acids in the waste stream. Tar acids are actually made up of roughly 60 to 80 percent phenol, the remainder being mostly cresol with small amounts of some higher homologs of phenol.[6,28] The phenol concentrations in WAL commonly cited as design values are 1,000 to 2,000 parts per million.

Several phenol removal/recovery techniques are practiced or have been tried. The traditional process types are solvent extraction and steam stripping. In both cases the phenol-rich phase, once extracted, is treated with caustic to make sodium phenolate. Carbon adsorption is a process which has been considered but is not yet in full scale use. In addition to the above, some sort of final wastewater treatment (perhaps biological) is probably necessary to make the waste acceptable for discharge.

The widely used solvent extraction dephenolization process generally utilizes light oil or benzene to extract phenol from the waste ammonia liquor. In addition, several proprietary solvents have been used over the years. These solvents are generally more expensive than light oil and require additional effort to recover the solvent in order to be economical. They have not been widely used in the United States. The efficiency of the solvent extraction process is generally around 95 percent phenol removal, although some plants have done better and by increasing the solvent rate or improving the contactor efficiency better removal can be effected. Solvent extraction removes all of the tar acids with good efficiency. Figure 7 includes a flow diagram of a solvent extraction dephenolization process. The flow of weak ammonia liquor is into and down through an absorber column. This absorber column may be a packed tower, a tray tower, a mechanically agitated column, or a series of mixer-settlers. The solvent rate is generally on the order of 1.2 volumes of solvent per volume of weak ammonia liquor, although wide variations in practice are to be expected.

The purpose of the caustic contactor is to remove the phenol from the light oil by converting it to sodium phenolate. Again, the contactor may be either a packed tower or mixer-settler. Consumption of caustic is in the

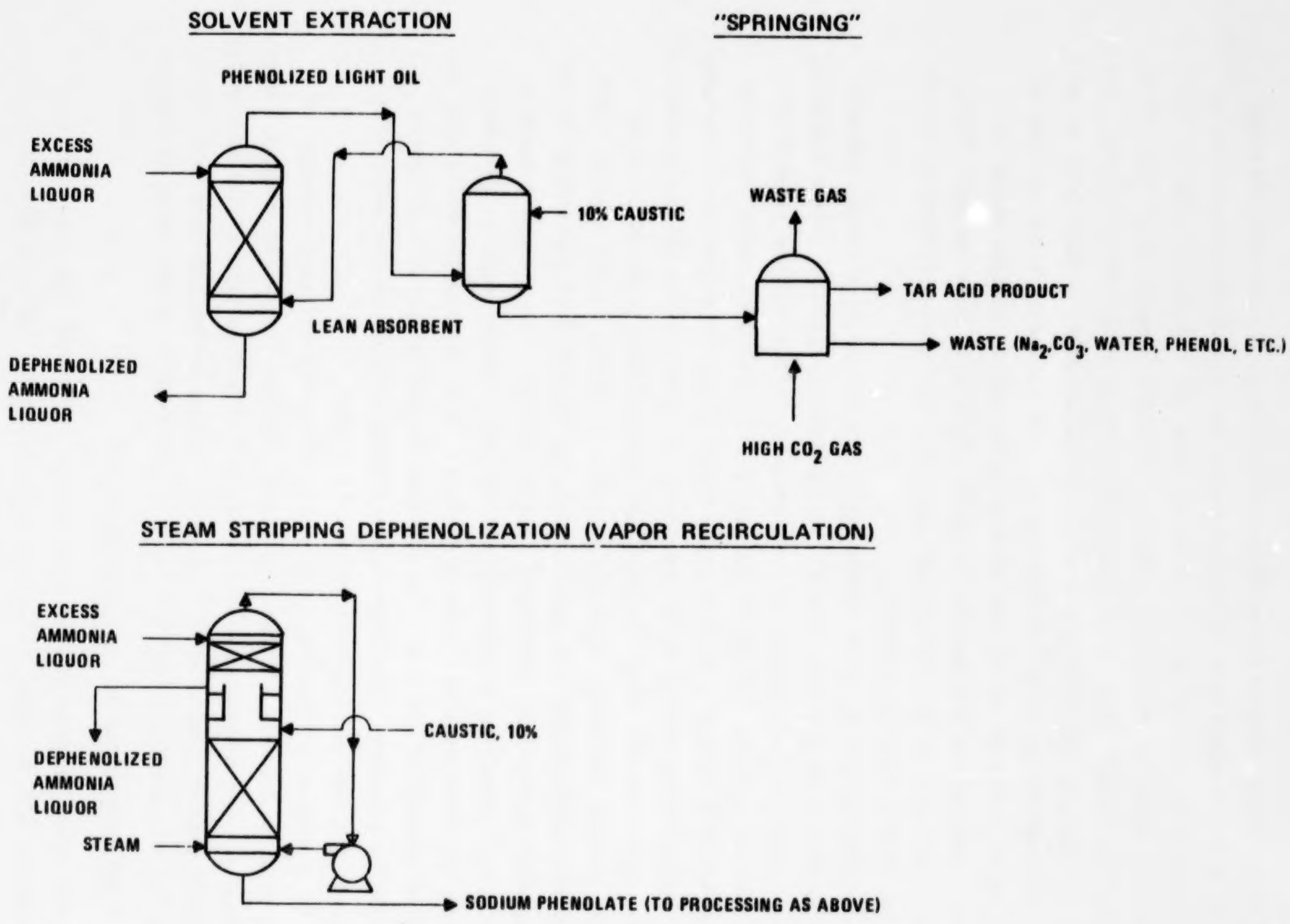

SOLVENT EXTRACTION
"SPRINGING"
PHENOLIZED LIGHT OIL
EXCESS AMMONIA LIQUOR
10% CAUSTIC
WASTE GAS
TAR ACID PRODUCT
LEAN ABSORBENT
WASTE (Na_2CO_3, WATER, PHENOL, ETC.)
DEPHENOLIZED AMMONIA LIQUOR
HIGH CO_2 GAS
STEAM STRIPPING DEPHENOLIZATION (VAPOR RECIRCULATION)
EXCESS AMMONIA LIQUOR
CAUSTIC, 10%
DEPHENOLIZED AMMONIA LIQUOR
STEAM
SODIUM PHENOLATE (TO PROCESSING AS ABOVE)

Figure 7. Dephenolization.

range of twice stochiometric, although better results have been obtained. Caustic is often added as a 10 percent solution; the caustic operation is usually batch or semi-batch. In today's operation the phenol removal process usually stops at this point; that is, with the separation of the sodium phenolate solution. When it is desirable to recover the phenol itself, the phenol is removed from the sodium phenolate solution by contact with an acid gas. This operation is called "springing", and it leads to the release of phenol as a liquid on top of the aqueous phase and an aqueous waste of sodium carbonate and bicarbonate in water, along with some residual phenol. The acid gas used in the "springing" operation has generally been a combustion gas with a high CO_2 content.

Dephenolization by steam stripping is the second traditional process. It is sometimes called vapor recirculation dephenolization. Steam stripping of phenol must follow removal of free ammonia, as the ammonia is more volatile than the phenol. Figure 7 includes a flow plan of a vapor recirculation contacting device. The stripping steam is run in a loop which includes a stripping contractor in which the phenol is removed from the waste ammonia liquor, and a caustic tower in which the phenol-laden steam contacts an aqueous caustic solution. Sodium phenolate is formed in the caustic tower. The phenol stripper and the caustic contactor may be both physically in one column with appropriate internals, or they may be in two separate vessels. Under normal operating conditions, this process removes most of the phenol, but not the heavy homologs such as cresols. Thus its overall efficiency for tar acid removal is limited. The absorber is generally run a bit above atmospheric pressure. The steam recirculation rate is on the order of a kilogram of steam per kilogram of ammonia liquor.

As discussed previously, carbon absorption has not been reported as being used in the United States for phenol removal from waste ammonia liquor, although its use has been piloted by Republic Steel as part of the wastewater treatment process (not phenol recovery). Carbon absorption does have the potential of removing essentially all of the phenols in the waste stream.

4.5 FINAL COOLER AND NAPHTHALENE PROCESSING

The basic function of the final cooler is to cool the coke oven gas from around 60°C to about 25°C in order to improve light oil absorption in the light oil scrubber. As the gas is cooled, some water and most of the naphthalene which is still in the coke oven gas is condensed into the cooling medium. Both must be removed from the gas to prevent problems downstream.

The final cooler itself is often a simple spray tower. Packed towers can be used but condensed naphthalene may plug the tower. Spray towers require higher liquid rates or taller towers due to a lower contacting efficiency than is possible in packed towers.

The cooling medium has traditionally been water, but wash oils can also be used. If wash oil is the cooling medium, naphthalene will dissolve along with some light oil. The water which is condensed must be removed in a decanter and the wash oil recirculated and cooled. A slipstream of the rich wash oil is routed to the light oil plant for removal of the light oil and naphthalene. A lean wash oil make-up stream is provided to the final cooler circuit.

Final cooler cooling water may be either recirculating or once-through. Recent practice tends towards recirculation due to water pollution constraints. Naphthalene can be removed from the final cooler cooling water as a solid or it may be dissolved in tar in a sump and the water allowed to separate by gravity. Figure 8 is a flow diagram of a final cooler and recirculating water circuit with the naphthalene collected by physical separation. After contacting the coke oven gas in the final cooler, the water is pumped to a separation device prior to the cooling tower. Water soluble compounds such as chlorides and cyanide accumulate in the water. Naphthalene will separate by gravity in a sump, or the separation may be enhanced with a froth flotation separator or similar equipment. The naphthalene may then be skimmed from the surface of the water.

After separation of the naphthalene, the water is commonly cooled in an atmospheric cooling tower and then recirculated to the final cooler. The use of a cooling tower ties the conditions in a final cooler to weather conditions at the plant site, and during hot, humid summer weather 30°C would be difficult to maintain. During the winter a cooling system designed for summer conditions is oversize, and the cooling tower will be lightly loaded. The operation of the cooling tower is of interest because the cooling tower will strip out the light components dissolved in the recirculating

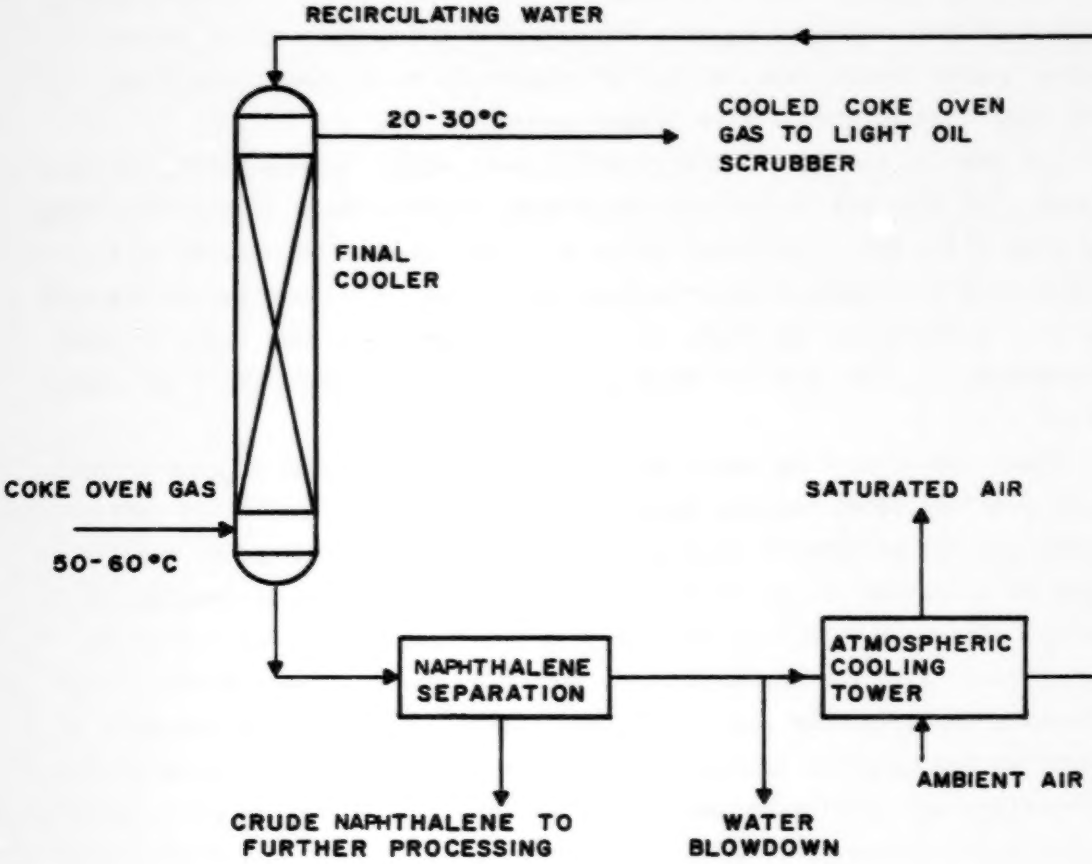

RECIRCULATING WATER
20-30°C
COOLED COKE OVEN GAS TO LIGHT OIL SCRUBBER
FINAL COOLER
COKE OVEN GAS
50-60°C
SATURATED AIR
NAPHTHALENE SEPARATION
ATMOSPHERIC COOLING TOWER
AMBIENT AIR
CRUDE NAPHTHALENE TO FURTHER PROCESSING
WATER BLOWDOWN

Figure 8. Final cooler with naphthalene separation.

water. The extent to which these are dissolved in the water and then stripped into the air is dependent on the operation of the final cooler and cooling tower. A blowdown stream is taken from the recirculating water to dispose of water condensed from the coke oven gas and not evaporated or entrained in the cooling tower. Some blowdown is necessary to dispose of chlorides.

Naphthalene collected by physical separation is impure, having a dirty brown appearance and containing a good bit of water (perhaps 50-60 percent). This naphthalene slurry is commonly dewatered by gravity separation as much as possible. Further processing may include drying/melting with non-contact steam for sale as crude naphthalene or refining into a better grade of naphthalene.

The second common way of handling the final cooler water is to pass the water through tar in the bottom of the final cooler and allow the naphthalene to dissolve in the tar. The naphthalene is then included with the tar in any additional refining operations. The tar, of course, contained considerable naphthalene before including the final cooler naphthalene. Figure 9 is a flow diagram of a tar bottom final cooler. There must be sufficient water above the tar bottom to force the water through the distributer and into the tar. The water then separates by gravity and is decanted. The tar is recirculated back to the tar storage tanks continuously. Obviously, the same operation could be conducted in separate vessels of various designs. The efficiency with which naphthalene is removed by the tar was not available in the literature although it is apparently fairly high. The final cooler water is cooled in a cooling tower and recirculated to the top of the tower. Again, air stripping of light components in the water occurs to some extent in the cooling tower. A significant water blowdown is again necessary.

4.6 LIGHT OIL RECOVERY

Light oil is a clear yellow-brown oil, with a specific gravity of about 0.86. It is the coke oven gas fraction in which the more than 100 constituents with boiling points between 0°C and 200°C or so reside. Benzene is generally 60 to 85 percent of light oil, with toluene (6 to 17 percent), xylene (1 to 7 percent), and solvent naphtha (0.5 to 3 percent) being the more important of the lesser constituents. Crude light oil production

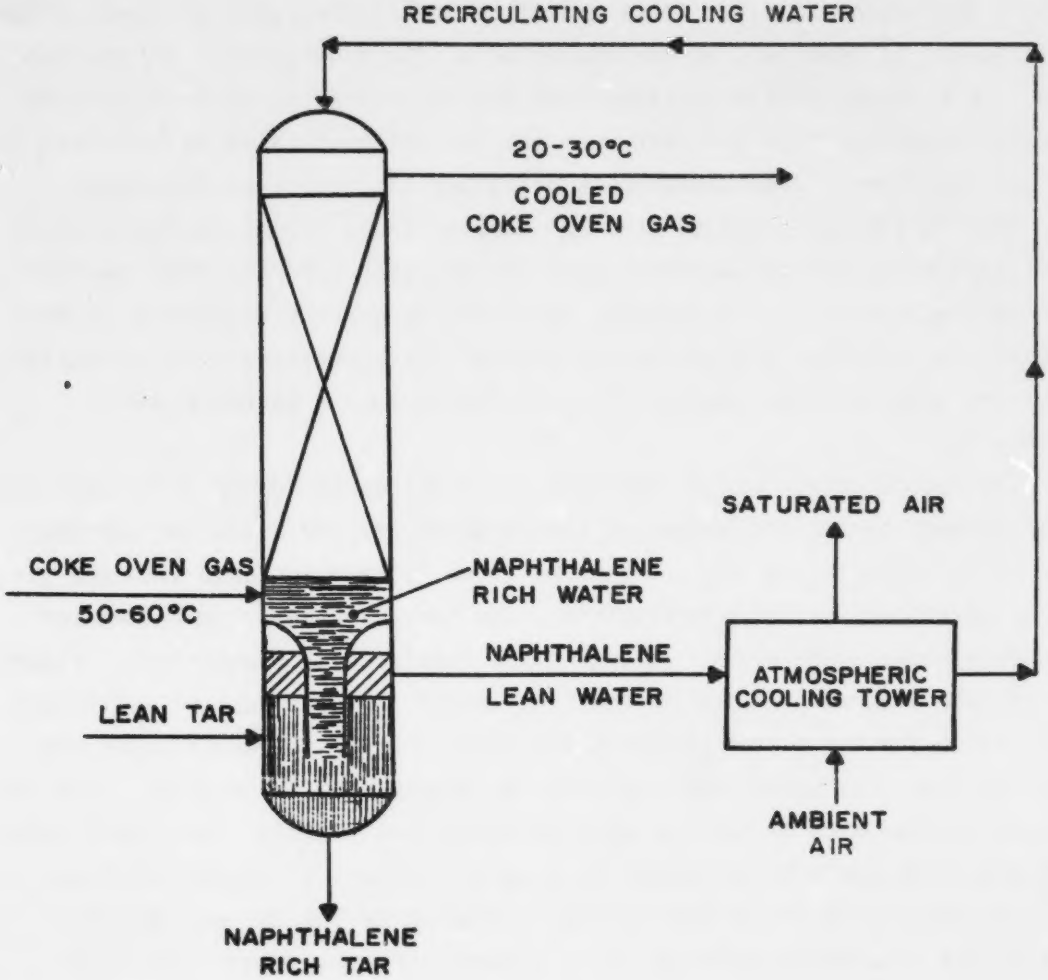

RECIRCULATING COOLING WATER
20-30°C
COOLED COKE OVEN GAS
SATURATED AIR
COKE OVEN GAS
50-60°C
NAPHTHALENE RICH WATER
NAPHTHALENE LEAN WATER
ATMOSPHERIC COOLING TOWER
LEAN TAR
AMBIENT AIR
NAPHTHALENE RICH TAR

Figure 9. Tar-bottom final cooler.

averages slightly less than one mass percent of the coal carbonized, or 14.4 l/Mg coke.

There are basically three available collection processes for light oil:

1. absorption in a liquor (wash oil), followed by steam stripping to separate the light oil;
2. refrigeration followed by compression at conditions of -70°C and 10 atmospheres;
3. adsorption on solids (such as carbon), followed by regeneration.

After separation light oil may be sold as crude light oil or it may be further fractionated on-site into various light oil fractions.

The absorption of light oil into wash oil is prevalent in the United States. Figure 10 is a flow plan of a fairly typical process. Wash oil towers may be operated singly, or as two or more in series with countercurrent flow. They may be tray or packed towers or of the gravity spray type. The spray towers are less likely to plug, but are less efficient for a given tower height and oil rate. Wash oil is kept above the coke oven gas temperature to prevent condensation of water (which emulsifies). At about 30°C a traditional light oil scrubber will remove around 95 percent of the light oil from coke oven gas. Wash oil is circulated at around 1.5-2.5 l/m^3 coke oven gas through the contacting stages.

The benzolized wash oil is steam stripped to recover the light oil. Live steam is injected into the bottom of a plate tower and the more volatile light oil is stripped overhead. One of the main criteria for selection of a wash oil is that a good separation be achieved with minimal degradation of the wash oil. The flow plan in Figure 10 shows light oil recovery and subsequent rectification to separate a benzene-toluene-xylene (BTX) fraction from the heavier components. A simpler flow scheme would leave out the rectifier, collecting a crude light oil fraction.

Further refining of light oil into high purity fractions such as benzene, toluene, and xylenes is practiced at some plants. The light oil is fairly valuable, but the adverse economics of small-scale refining have forced many plants to shut down or not replace light oil fractionation equipment. In addition to the fractionation, the light oil fractions must be desulfurized before sale on the open market. Treatment with sulfuric acid is the accepted

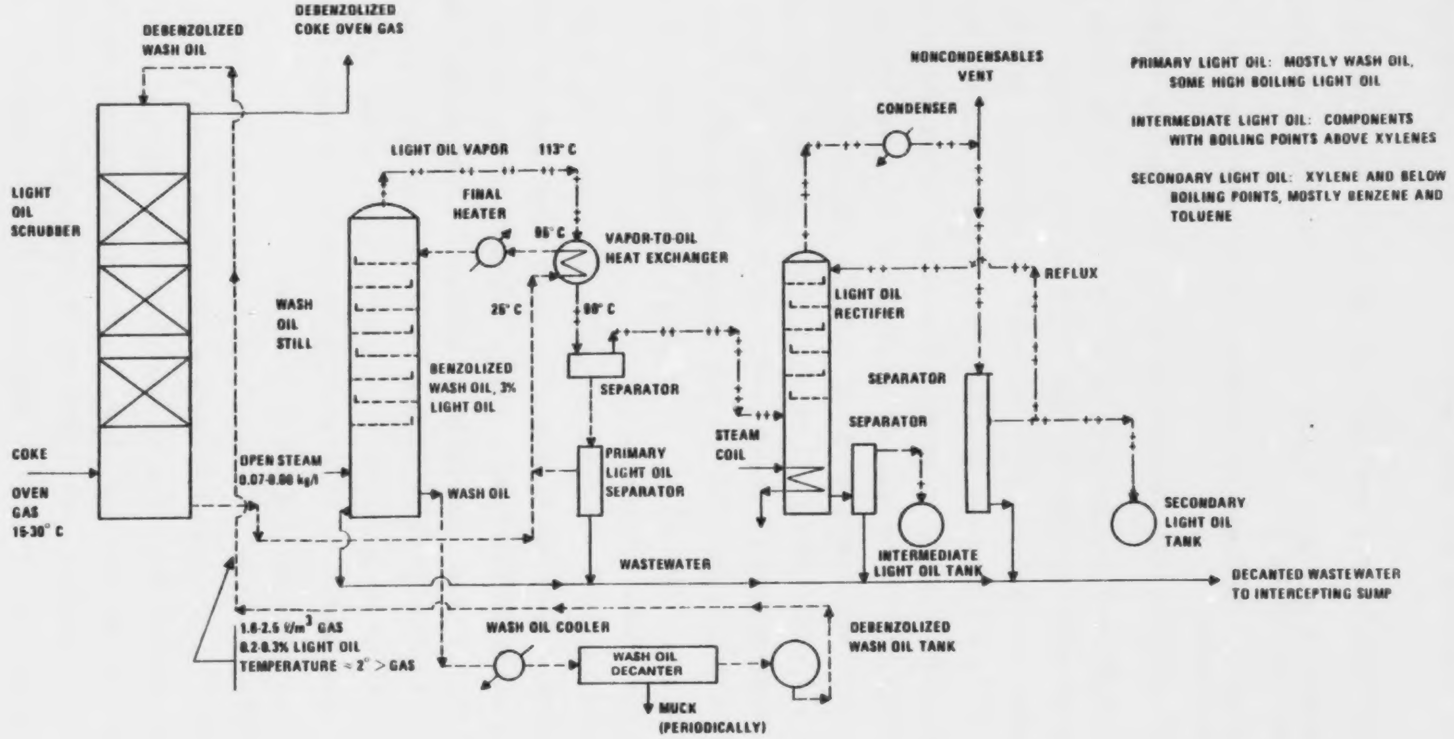

DEBENZOLIZED WASH OIL
DEBENZOLIZED COKE OVEN GAS
LIGHT OIL SCRUBBER
COKE OVEN GAS 15-30° C
WASH OIL STILL
OPEN STEAM 0.07-0.08 kg/l
LIGHT OIL VAPOR
113° C
FINAL HEATER
95° C
VAPOR-TO-OIL HEAT EXCHANGER
25° C
90° C
BENZOLIZED WASH OIL, 3% LIGHT OIL
WASH OIL
SEPARATOR
PRIMARY LIGHT OIL SEPARATOR
WASTEWATER
1.6-2.5 ℓ/m³ GAS
0.2-0.3% LIGHT OIL
TEMPERATURE ≈ 2° > GAS
WASH OIL COOLER
WASH OIL DECANTER
MUCK (PERIODICALLY)
DEBENZOLIZED WASH OIL TANK
STEAM COIL
LIGHT OIL RECTIFIER
CONDENSER
NONCONDENSABLES VENT
SEPARATOR
SEPARATOR
REFLUX
INTERMEDIATE LIGHT OIL TANK
SECONDARY LIGHT OIL TANK
DECANTED WASTEWATER TO INTERCEPTING SUMP
PRIMARY LIGHT OIL: MOSTLY WASH OIL, SOME HIGH BOILING LIGHT OIL
INTERMEDIATE LIGHT OIL: COMPONENTS WITH BOILING POINTS ABOVE XYLENES
SECONDARY LIGHT OIL: XYLENE AND BELOW BOILING POINTS, MOSTLY BENZENE AND TOLUENE

Figure 10. Wash oil absorption of light oil with light oil rectification (derived from Wilson and Wells[6]).

process. After the acid wash, caustic is used to neutralize the acid and the oil is separated from the aqueous waste.

Light oil refining on-site is often batch or semi-continuous, as the practice reduces cost and increases the unit's flexibility. Products include the forerunnings, benzene of various purities, as well as toluene and xylene, washed solvent naphtha, and crude solvent naphtha.

Catalytic refining and/or hydrodesulfurization have been utilized at a number of plants to produce very high purity benzene. The processes were apparently successful but have not become widespread, possibly for economic reasons.

4.7 SULFUR HANDLING

The sulfur in coke oven gas exists as H_2S and the organic sulfur compounds (primarily carbon disulfide, CS_2, and carbonyl sulfide, COS). A fairly typical coking coal might contain about 1 percent sulfur, and about half the sulfur remains in the coke after carbonization. Perhaps 95 percent by volume of the sulfur in the coke oven gas is in the form of H_2S; of the remainder, CS_2 accounts for 3.5 percent and COS for 1.5 percent.

Sulfur is of concern in coke oven gas because it is emitted as SO_2 when the coke oven gas is burned. Desulfurization has a long history, as sulfur was once removed from gas for residential use by contact with iron oxide. With the advent of natural gas in the 1950's, desulfurization became much less common. Industrial fuel gas has not commonly been desulfurized, but the recent natural gas shortages and price increases are causing reevaluation.[29] Desulfurized coke oven gas could serve as the primary sulfur-free fuel source, at a price controlled by the steel producer. National standards for sulfur emissions due to coke oven gas combustion have not been issued. The desulfurization facilities commissioned in this decade have been in response to state or local standards.

On the surface coke oven gas desulfurization appears to be very similar to desulfurization of some oil refinery streams, the technology for which is well developed. Coke oven gas contains hydrogen cyanide, however, which is a serious obstacle; many processes cannot be used. Cyanide is mentioned below, but most of the relevant comments on cyanide have been gathered in a later section.

The distinction between organic sulfur and hydrogen sulfide is of some interest because the desulfurization of coke oven gas rarely removes organic sulfur. (The Sulfiban process is an exception.) Thus, the more completely H_2S is removed the more organic sulfur dominates what remains.

Process Alternatives

Leaving aside the outmoded use of iron oxide, there are essentially two categories of process steps to achieve desulfurization of coke oven gas: absorption of acidic gases in a basic solution, or absorption of reducing gases in an oxidizing solution. Hydrogen sulfide is acidic, but so also are HCN and CO_2. HCN is less completely absorbed because it is a weaker acid and CO_2 absorption is impeded by slow reactions.[30,31] Co-sorption of CO_2 merely increases the amount of base which must be circulated and the heat required to regenerate it, but the unavoidable absorption of HCN creates problems for downstream sulfur processing.

Hydrogen sulfide is a reducing agent but so are HCN, CO, COS, and CS_2. The last three are only sparingly soluble, so that these components of the gas have little access to the oxidizing agent in the liquor phase. Future catalyst developments may solve the problem of HCN interference, but it is this nuisance which prevents the easy adaptation of technology originally developed for sweetening natural gas and later applied to refinery gas.

Whatever the technique for removing sulfur from the coke oven gas, the eventual disposal of the sulfur compounds is important. All of the modern processes involve a regeneration step to recover process chemicals in which the sulfur is separated again from the absorbent. In many cases a concentrated acid gas stream containing H_2S is formed. The preferred way of handling this stream is generally a Claus sulfur plant or production of sulfuric acid by the contact process. Other processes regenerate by forming elemental sulfur. Emissions from the regeneration step may be important and must be examined.

Absorption in Basic Solutions

Three fully commercial processes for desulfurizing with a basic agent are the vacuum carbonate process, developed by Koppers about 1940[30]; the Sulfiban process employing ethanolamine, adapted for present purposes by

Bethlehem Steel and Black, Sivalls, and Bryson early in this decade; and the ammonia absorption process of Firma Carl Still.[32]

Vacuum Carbonate--

Koppers' vacuum carbonate process enjoyed practically a monopoly in U.S. plants until Sulfiban, according to a 1974 inventory.[33] Dravo/Still is a more recent entry in the race. Not to be outdone by the superior performance claimed for Sulfiban units, Koppers has recently responded with a "two-stage" version of a vacuum carbonate,[34] based perhaps on Shoeld's patent,[35] as shown in Figure 11. The classical, one-stage, version can be identified with those portions of the absorber and stripper (traditionally called an "actifier") labeled "primary". The circulating carbonate trickles down through the packed absorber, removing H_2S from the gas. It is then pumped up and trickles down through the stripper, losing H_2S to steam, and is returned to the absorber. The acid gas is routed to a Claus plant or sulfuric acid plant for recovery of the sulfur. In the new version a portion of the circulating carbonate leaving the primary stripper is returned, to trickle down through a secondary stripper for more vigorous regeneration. This doubly stripped absorbent then is pumped to the top of the secondary absorber, where it contacts coke oven gas already treated in the primary absorber.

Ammonia, tar, and naphthalene removal must be completed ahead of the carbonate plant. Ammonia must be kept below 200 ppm, or it will cause problems in the Claus plant after passing through the vacuum carbonate process.[36] Tar and naphthalene will accumulate and foul the carbonate plant.

The stripper is operated at a high vacuum (10 cm Hg absolute). Contact condensers are generally used on the stripper vapor to reduce fouling problems. Secondary reactions occur in the absorber, making a purge necessary to remove thiocyanate and thiosulfate salts.

The performance of the absorber in this service is governed by the choice of packing, its depth, the absorbent temperature, and composition, the ratio of absorbent flow to gas flow, and the column cross-section per unit of gas flow. These factors can be broken down into two sets: those determining the local driving force for mass transfer (temperature, composition, and flow rates), and those determining the resistance to mass transfer

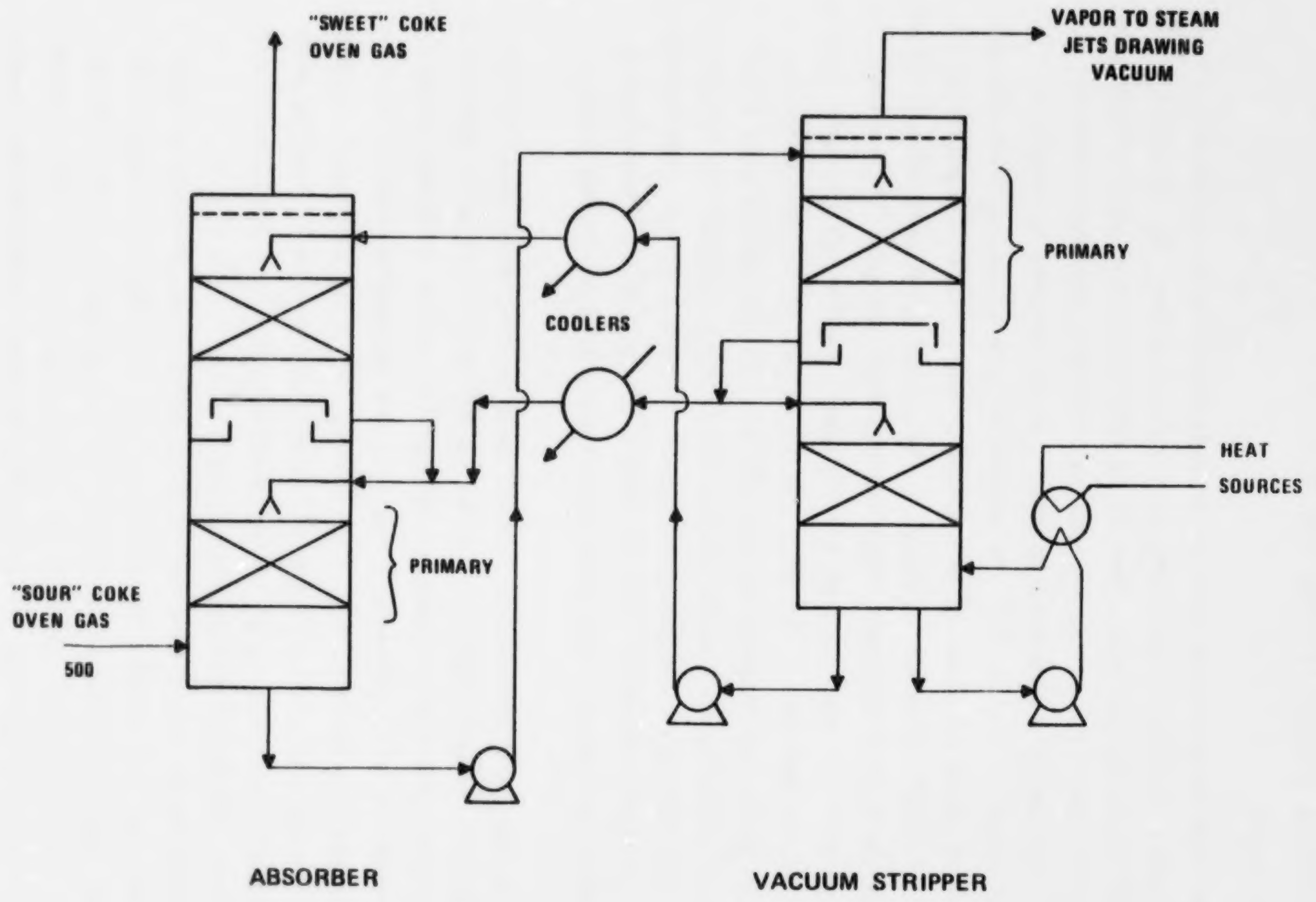

"SWEET" COKE
OVEN GAS
VAPOR TO STEAM
JETS DRAWING
VACUUM
COOLERS
PRIMARY
PRIMARY
HEAT
SOURCES
"SOUR" COKE
OVEN GAS
500
ABSORBER
VACUUM STRIPPER

Figure 11. Koppers' two-stage vacuum carbonate process.

(packing, depth, flow per unit area). Cooling and a high ratio of liquid to gas improve the driving force in the absorber. Thus, if the primary absorber were in all respects a duplicate of the single classical absorber, the addition of more packing served with leaner absorbent (even though with somewhat less absorbent) is bound to improve collection efficiency. The same goal could have been accomplished, without resort to double staging, by increasing the depths of both absorber and stripper and supplying more steam to the latter. There is a presumption, however, that the two-stage arrangement is more economical.

Certainly one feature of the new version is steam economy. Instead of using fresh steam for the stripper, steam is derived by boiling the lean absorbent. Since the absorber is under vacuum, the heat sources can be at a relatively low temperature. Koppers recommends that the flushing liquor and the steam from the ejectors serving the vacuum absorber be used as heat sources.

Sulfiban--

The Sulfiban process and its antecedents have been adequately described in the literature[30,32,37,38] and will only be summarized here. Improved basic data have recently been published.[39] One could wish, however, for reports from the two operators (Shenango, Jones and Laughlin) who have less of a stake in the commercial success of this technology.

The Sulfiban process employs the conventional arrangement of an absorber and a reboiled stripper. The absorbent is 13-18 percent mono-ethanolamine (MEA) in water. Vapor for stripping at atmospheric pressure is generated in a steam-heated reboiler. (It has never been made plain why the carbonate absorbent is regenerated under vacuum, while MEA is not. The arguments concerning utilities consumption apply as well, qualitatively, to both.) Again, the acid gas must be treated to recover the sulfur. The buildup of stable by-products in the absorbent requires that about two percent of the absorbent inventory be purged daily to a "reclaimer"; similarly, the buildup of ammonium salts in the stripper condensate, which is normally refluxed to the stripper to prevent amine losses, is controlled by purging to the weak ammonia liquor.[38]

The older literature[14,30] contains repeated assertions that alkanolamines are degraded by the HCN and COS in coke oven gas. The proponents of Sulfiban claim that this reputation is undeserved,[37] and have been supported by experience at the full scale unit of Bethlehem Steel.[40] Indeed, among processes for absorption in basic reagents only Sulfiban absorbs significant fractions of the COS and CS_2 in the gas. Since these also form SO_2 when the gas is burned, a process which removes them from the gas need not absorb as much of the H_2S to meet a standard which, like Pennsylvania's, limits total sulfur emissions.

Dravo/Still--

A rule of thumb in chemical process synthesis is to avoid introducing extraneous agents. Consistent with that philosophy, one might explore the removal of H_2S with ammonia liquor,[30] and in fact this is the basis of a range of process options offered by Firma Carl Still[32] and marketed in this country by Dravo. Let us examine the process variant, shown in Figure 12, which Dravo has installed for Armco at its Middletown, Ohio, plant. Anhydrous ammonia and sulfuric acid are the products and as described, this is a combination of two processes (USS PHOSAM and Dravo/Still) which could be considered independently for ammonia and sulfur removal respectively. (The description is based primarily on vendors' brochures and it is in part conjectural.)

The coke oven gas is treated to remove acid gases (H_2S, HCN, and inevitably some CO_2) and ammonia in that order. The absorbent in the H_2S scrubber is aqueous ammonia, in such volume and strength as will lower the sulfur content to the desired range. (COS and CS_2 are little affected.) As shown in Figure 12, the ammonia content of the absorbent derives from condensing a wet ammonia vapor elsewhere in the system; but water from various sources could be added to this stream.

When sodium carbonate is used to scrub coke oven gas, the acid constituents removed from the gas are replaced by a comparable amount of innocuous CO_2. Here the raw gas is enriched in NH_3, which is normally removed by H_2S. The remedy is to reverse the order, to remove NH_3 after H_2S. The agent of choice is phosphoric acid with a relatively small amount of ammonia left in it after regeneration; it can be thought of as aqueous $(NH_4)H_2PO_4$.

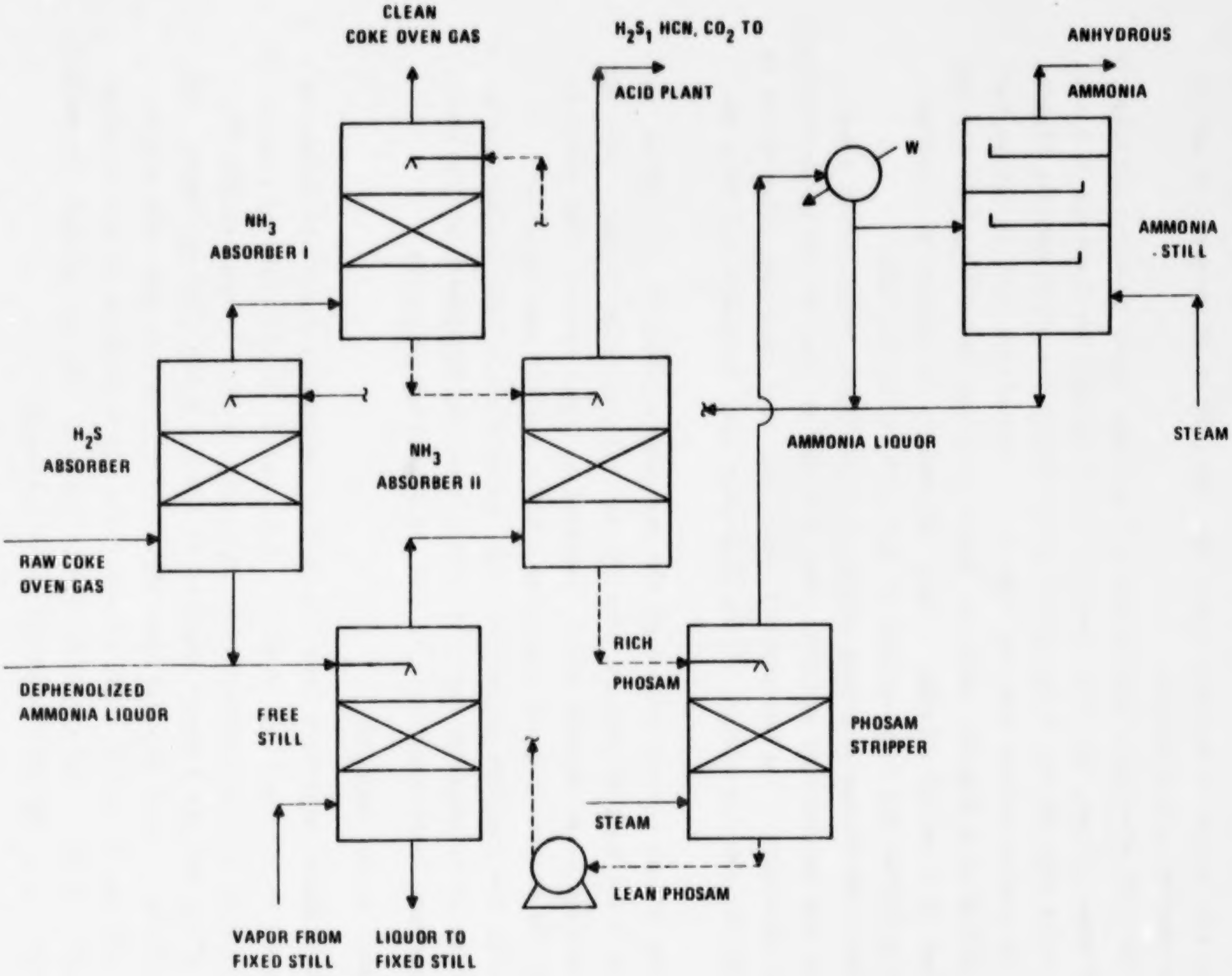

CLEAN
COKE OVEN GAS
H_2S_1 HCN, CO_2 TO
ACID PLANT
ANHYDROUS
AMMONIA
W
NH_3
ABSORBER I
AMMONIA
.STILL
H_2S
ABSORBER
NH_3
ABSORBER II
AMMONIA LIQUOR
STEAM
RAW COKE
OVEN GAS
RICH
PHOSAM
DEPHENOLIZED
AMMONIA LIQUOR
FREE
STILL
PHOSAM
STRIPPER
STEAM
LEAN PHOSAM
VAPOR FROM
FIXED STILL
LIQUOR TO
FIXED STILL

Figure 12. Dravo/Still processing.

This is the so-called "Phosam" absorbent developed by U. S. Steel and first commercialized by them at the Clairton Works in 1968. Since modest amounts of NH_3 are tolerable in the cleaned gas, the degree of recovery is set by the economics of the process.

The rich absorbent leaving the H_2S absorber could be steam-stripped in a dedicated column, but this function can reasonably be combined in a new plant with that of the "free still" which treats the crude ammonia liquor.

The vapors rising from the free still, containing most of the sulfur and considerable ammonia, meet the Phosam solution descending from the NH_3 absorber in a second absorber. Here the ammonia is removed to a degree which satisfies the requirements of the sulfuric acid plant.

The rich Phosam absorbent passes to a stripper, where direct steam removes the accumulated ammonia. The stripped or lean Phosam is recirculated to the absorbers. The wet ammonia vapor goes to a condenser, from which is derived the ammonia content of the absorbent used to remove H_2S from the gas.

The Phosam circuit processes all the ammonia used for absorption, as well as a net make of ammonia from the raw gas and crude liquor. This net is forwarded to an ammonia still, operated at about 12 bars (180 psia) to permit the condensation of anhydrous ammonia against cooling water.

With the possible exception of the ammonia still, the optimal design of all these units requires explicit recognition and management of the several simultaneous ionic equilibria in the liquids being processed.

Cryogenic Sulfur Recovery--

A dramatic departure from the kind of technology described above was announced in 1972 by U. S. Steel.[41] A cryogenic desulfurization process was installed at their Clairton Works. Hydrogen sulfide freezes at -82.9°C (-117.2°F), and has a vapor pressure of about 0.2 bar (150 mm) there. But since there is much less H_2S than this in the coke oven gas, the process cools the gas to -130°C (-220°F) where the vapor pressure of H_2S is below 0.004 bar (3 mm). Certain other constituents of the gas not earlier removed, especially CO_2, may also condense in this process.

Absorption of H_2S in Oxidizing Solutions

The solubility of H_2S in water is quite small. The aim of absorption in basic solutions is to convert the dissolved H_2S to the hydrosulfide ion, HS^-, making room for more H_2S. By contrast, the aim of oxidizing systems is to convert H_2S to elemental sulfur or to sulfite, thiosulfate, or sulfate ions. Various processes dating back to the turn of the century[42] sought not merely to desulfurize the gas but often to make the sulfuric acid required in the ammonia saturators.

Thylox--

Perhaps the most important of these forerunners is the Thylox process, first commercialized by Koppers in 1926. The process, as described by one of the inventors,[14] involves the displacement of oxygen from a thio-arsenate moiety by H_2S in a nearly neutral solution:

$$Na_4As_2S_5O_2 + H_2S \rightarrow Na_4As_2S_6O + H_2O.$$

This is followed by the regeneration and simultaneous froth flotation of sulfur product upon blowing with air:

$$Na_4As_2S_6O + 1/2O_2 \rightarrow Na_4As_2S_5O_2 + S.$$

The finely divided sulfur product, with unobjectionable levels of arsenic for the purpose, found a market as an insecticide. The subsequent invention of more powerful and specific insecticides has foreclosed this market. Since arsenic contamination is a liability in other end uses for sulfur, Thylox and an analogous modern process (Giammarco-Vetrocoke) have lost ground.

Stretford--

Many of the same principles are found in the Stretford process, which has been commercialized in this decade at a Canadian coke plant.[43] The chemistry, while not thoroughly understood, employs vanadium in a higher valence state to oxidize H_2S to elemental sulfur. In a separate device, air blowing re-oxidizes the vanadium, with the help of an organic oxygen carrier, and makes a froth of the fine sulfur.

Takahax--

A family of processes pioneered in Japan by Nippon Steel, and recently commercialized in this country by Ford, Bacon and Davis--Texas, is called

Takahax. Here the organic oxygen carrier dissolved in a basic absorbent becomes the main oxidant; the metal salts are dispensed with. In the version to be operated at Kaiser Steel, called Takahax-A,[44] ammonia is the base and the chosen carrier is 1,4-naphthoquinone-2-sulfonic acid. It appears that this carrier was chosen deliberately for its greater oxidizing power, the object being to form not elemental sulfur but soluble sulfur-bearing anions which may feasibly build up in the circulating absorbent. A portion of this strong solution is purged to wet-air oxidation, at conditions of 60 bars (880 psia) and 200°C or above. Here the catalyst is destroyed, the sulfur species are converted to sulfuric acid, and any nitrogen emerges as a gas or as ammonium ion. This product is sent to the saturator to be used in ammonia recovery.

4.8 CYANIDE TREATMENT

Hydrogen cyanide, commonly called cyanogen in the coking industry, is a minor but troublesome component of coke oven gas. No attempt is made to collect it as a by-product, but the disposition of HCN and its salts in a by-product plant is important both environmentally and with respect to desulfurization processes. The mode of cyanide formation during coking is obscure; indeed there is probably more than one route. Whatever the route, HCN appears in the collection mains and is quenched. It is a weak acid, so that some dissolves in the ammonia liquor, but most of it stays with the gas. Most of that which dissolves is stripped out in the free ammonia still and is returned to the gas. Normal operation of the free still does not remove cyanide aggressively; some reaches the fixed still (if present and operating) where it becomes fixed as calcium or sodium cyanide in the waste ammonia liquor. From there it goes to wastewater treatment or to the receiving waters.

The pH of the excess ammonia liquor is mildly basic, say 9, but HCN is such a weak acid that little of it is ionized at this pH. Thus, it would be relatively easy to strip out in the free still if it were not so very polar. (Liquid HCN boils at 26°C and is miscible in all proportions with water.[45]) The motivation for operating the free still, and more especially the fixed still, has traditionally been the value of recovered ammonia. The fate of HCN was not important. In the base case considered in developing the effluent guidelines (Table 44 in Reference 46), conventional practice leads to a cyanide level of 90 mg/l (90 ppm) in the combined effluent of 730 l/kkg (175 gal/ton). Only 55 percent of the cyanogen is stripped out in the free still and scarcely any in the fixed still. Dunlap and McMichael assume only 40 percent removal.[47] Clearly it is not important which of these control efficiencies is more nearly correct; what matters is that neither is acceptable. It is just as clear that redesign of the free and fixed stills, with more plates, more steam, pH adjustment, or some combination of these,[48] could reduce NH_3, H_2S, and HCN in the waste ammonia liquor to any desired level. Other approaches may be preferable, to be sure.

The bulk of the cyanide, then, is found in the gas stream. Its fate there depends upon processing options. It is preferable that it should be deliberately destroyed, otherwise it may become an air pollutant.

Process Alternatives

Traditional Processing, with Ammonium Sulfate Production and No Desulfurization--

The coke oven gas passes through the tar removal step and a reheater, is blended with wet ammonia vapor (containing some HCN) from the free still, and passes to the saturator. Here ammonia is absorbed in sulfuric acid. There may be some hydrolysis of HCN; most of the cyanide, however, evidently passes through the saturator.

The next process unit, customarily, is the final cooler. The purpose is to cool and dehumidify the gas before it goes to light-oil scrubbing, and incidentally to remove naphthalene. The final cooler was historically served by once-through cooling water in direct contact with gas. Pressures from regulatory authorities have tended to reduce the volume and/or strength of effluents. One of the responses by the coking industry has been to shift from once-through water to recirculated water, with a cooling tower in the circuit. Some HCN dissolves in the water in this arrangement; data for Bethlehem's Lackawanna plant[49] attest that on the order of 50 percent enters the water. Other versions have used water and tar jointly (so that the naphthalene is returned to the tar), wash oil,[49] or indirect cooling. The inlet water temperature varies seasonally, and the water rate is adjusted with the season, less being required in the winter. The absorption of HCN is inevitable but is not a criterion of performance. The amount absorbed varies seasonally and is difficult to anticipate.

We may gain some quantitative grasp of the problem from published analyses of waste loadings in coke plants. "Plant D" in the EPA Development Document[46] employed once-through cooling water, which was evidently the largest component of total raw waste load of 19,200 liters per 1000 kg of coke. The cyanide content was 7.7 mg/l, for an aggregate cyanide output of 150 g/kkg or 0.015 percent. Comparable numbers for Plants A, B, and C are 0.006, 0.006, and 0.002 percent. Not all of these amounts come from the final cooler, of course, The circumstances of Plant D, direct cooling with once-through water, suggest that this is the most cyanide which will be removed from the gas (discounting seasonal variations). Previously it was shown that domestic coking coals are remarkably uniform in their nitrogen content, and that a nearly invariant fraction of this nitrogen emerges with the coke. The ammonia production and the coking conditions thus lead us to anticipate that HCN production is fairly uniform at 0.05 percent. Clearly Plant D does not remove even the bulk of it, and the other three plants not as much, by this route.

What is the situation if the final cooler is served with recirculated water derived from a cooling tower, possibly dedicated to this service?

If only the water is considered, there are evaporative and drift losses and a blowdown to control hardness and/or corrosion. But from the standpoint of cyanide we now see an absorber (the gas cooler) and a stripper (the water cooler); most of the cyanide picked up by the cooling water will be discharged to the air. The temperature of recirculated cooling water cannot be below the dew point of the ambient air, and operating policy may restrict the termperature to, say, 15 to 30°C. But the point is that this temperature varies seasonally and is not unlike that of once-through water at the same site, so that the water rate and cyanide content will be comparable to those at Plant D. We conclude that a direct final cooler using recirculated water could easily emit HCN to the ambient air in the amount of 0.1-0.2 kg per Mg of coal.

What of the light-oil plant? Recall that the coke oven gas is contacted with a lean wash oil which, upon leaving the absorber loaded with light oil and containing some HCN[13], is routed to a stripping column. Where that column is served with open steam, the condensate separates into two layers: light oil and a sour water containing some HCN.[47] We must conclude that some HCN is not condensed and becomes an air pollutant at that point, but the amount is much more difficult to quantify. Since HCN is a polar molecule, much more soluble in water than in oil, we may guess that this source is small compared to that from the kind of cooling tower described earlier.

In many plants the gas leaving light-oil recovery is distributed to the coke-oven burners and other fuel consumers in the plant. Cyanogen is a nuisance in distribution systems, gas meters, gas holders, and burners[13] because it forms a corrosive acid at the dewpoint:

$$18HCN_{(aq)} + 7Fe_{(s)} \rightarrow Fe_7(CN)_{18(s)} + 9H_{2(g)}.$$

The salt, prussian blue, precipitates; it can also happen that when the line warms up and dries out the salt is carried along with the gas to where it blocks burner orifices, especially pilot lights.

Processing with Sulfur Recovery--

When desulfurization is practiced, HCN again makes its presence felt. This acid gas is almost completely absorbed by basic solutions, as in vacuum carbonate, Sulfiban, or Dravo/Still. (See Section 4.4.) When the absorbent is regenerated or "actified" the HCN joins the H_2S, to create problems in the Claus plant[49] or in the burners of a sulfuric acid plant.

Cyanogen is also a reducing gas. In Stretford and Takahax chemistry it dissolves and reacts with elemental sulfur to form thiocyanate ion:

$$HCN_{(aq)} + S_{(S)} + OH^-_{(aq)} \rightarrow SCN^-_{(aq)} + H_2O.$$

The alkalinity can be restored, but sodium or ammonium thiocyanate builds up until it must be purged. Even though Dominion Foundries and Steel (Dofasco) at its Hamilton, Ontario, plant practices water washing to remove HCN ahead of their Stretford plant, the necessity for purging remains.[43] Dofasco has recently attached a purge-treatment process devised by Holmes of U.K. and marketed in this country by Wilputte. Similar systems are offered by Woodall-Duckham, by Nittetsu Chemical[50] and, for the Takahax process, Nippon Steel.[44] The first three are essentially incineration processes which recover sodium and/or vanadium values as solids and recycle sulfur as H_2S to the inlet of the sulfur recovery system. The last employs wet-air oxidation to ammonium sulfate/bisulfate, which is recycled to the ammonia-recovery system.

Since a purge-treatment system seems to be required in order to cope with the buildup of thiosulfate (Section 4.4), it is problematical whether it is worthwhile to try to exclude HCN from the H_2S absorber. If HCN pretreatment is by water washing, as at Bethlehem's Sparrows Point Plant,[49] regeneration with air would create air pollution. If ammonium polysulfide scrubbing is practiced,[51] this absorbent must be purged; there is no known regeneration technique.

When finally the rich H_2S stream is to be made into something useful, there are two principal choices: elemental sulfur by Claus or other chemistry, or sulfuric acid by the contact process.

Since hydrogen cyanide is detrimental to the sulfuric acid process, the practice at Sparrows Point is to cool the acid gas and pass it through an absorber served with water. Some 90 percent of the HCN is removed, and the water is heated and stripped with sweet coke-oven gas destined to be burned under the coke ovens.[52] Although Sparrows Point has gone to the Claus process for sulfur recovery, this water wash is still operated.[49]

Cyanogen causes corrosion and blockage in Claus plants,[49] so Bethlehem has demonstrated a remedy: the acid gas from its vacuum carbonate units at Burns Harbor and Lackawanna is passed over a "destruct reactor," an extra bed of Claus catalyst installed before the Claus burner. Here, in a series of reactions which are jointly exothermic, HCN and oxygen disappear; and ammonia, carbon monoxide, carbonyl sulfide, and carbon disulfide appear in the outlet.[49] Probable reactions are as follows, all compounds being gaseous:

$$\begin{aligned} HCN + H_2O &\rightarrow NH_3 + CO \\ 2CO + O_2 &\rightarrow 2CO_2 \\ CO + H_2O &\rightarrow CO_2 + H_2 \\ CO_2 + H_2S &\rightarrow COS + H_2O \\ COS + H_2S &\rightarrow CS_2 + H_2O. \end{aligned}$$

The first two reactions have a favorable free-energy change at all relevant temperatures. The last two reactions have weakly unfavorable equilibrium constants, but they can be driven by the excess of H_2S and the absence of organic sulfur in the feed. No one pretends that these are the elementary reactions. Rather, these reactants are chemi-sorbed on the Claus catalyst, dissociated in one or more stages to adsorbed free radicals such as $H\dot{C}O$ and HS·, rearranged, and desorbed.

4.9 WASTEWATER PROCESSING

Wastewater treatment is a necessary part of the coking operations, as raw coke oven gas contains water vapor driven from the coal in the coke oven. This water vapor is due to both surface moisture on the coal and bound water. Depending on coal type and coking practice, the flow of wastewater originating in the coke is around 100 to 200 l/Mg coke. Most of the water initially in the coke oven gas is condensed into the flushing liquor circuit described earlier. The blowdown from the flushing liquor circuit is known as weak ammonia liquor, and is the primary wastewater stream. Ammonia and phenols may be recovered from this stream. Once past the recovery sections, the water stream is waste ammonia liquor.

Wastewaters from other sources within the by-product plant are often combined with the waste ammonia liquor for treatment. These waste streams are highly dependent upon the processes used in the by-product plant. Some of them are unavoidable; others can be either greatly reduced or eliminated by proper choice of process technique. The major secondary sources of wastewater are:

1. barometric condenser water from steam jets used to draw vacuum on the ammonia crystallizer;
2. steam stripping waste from wash oil and light oil decanters;
3. blowdown from the final cooler.

In one sense, ammonia and phenol recovery from weak ammonia liquor are wastewater cleanup operations. However, they are being treated as by-product recovery processes, and this section deals only with operations downstream of ammonia and phenol recovery if these processes are used.

Weak (Waste) Ammonia Liquor

Flushing liquor contains tar, phenol, ammonia, and cyanide along with chlorides, sulfur compounds, and a host of hydrocarbons. Tar decanting removes most of the tar. As has been described, the blowdown from flushing liquor, excess ammonia liquor, goes through additional separation steps before phenol and ammonia are recovered. Table 10 presents a major component analysis of weak ammonia liquor prior to any recovery or clean-up process.

Following the decanters, weak ammonia liquor may be processed to recover phenols and ammonia. These operations have been discussed. Conventional phenol removal is 90-95 percent effective, and a free and fixed still combination can drop ammonia levels to around 150 mg/l, as well as stripping out most of the cyanide in the free still. In spite of these fairly high levels of removal, waste ammonia liquor requires additional treatment before being discharged to receiving waters.

Barometric Condenser Water

Barometric condenser water from vacuum ammonia crystallizers is a high volume wastewater (1000 l/Mg coke). The waste can be greatly reduced in volume by using surface condensers rather than barometric condensers. This step has led[23] to an order of magnitude reduction in rate. No literature reference has been found to the use of vacuum pumps to draw the low pressure on the crystallizer as a way of nearly eliminating this waste. Presumably the service is thought to be too severe. An attempt has been made to use recycled water in a cooling tower, but this system had problems with corrosion and pH control.

Intercepting Sump Water

Decanted water from the light oil plant is another large volume source of wastewater (300 l/Mg coke). This waste is primarily due to steam stripping of light oil from wash oil. The waste could be avoided by using reboilers for non-contact heating with steam. Extra attention would probably be

TABLE 10. MAJOR COMPONENTS OF WEAK AMMONIA LIQUOR[18,23]

	(mg/l)
Ammonia	5,000-6,000
Phenol	1,500-2,000
Cyanide	20-60
Oils	1,000

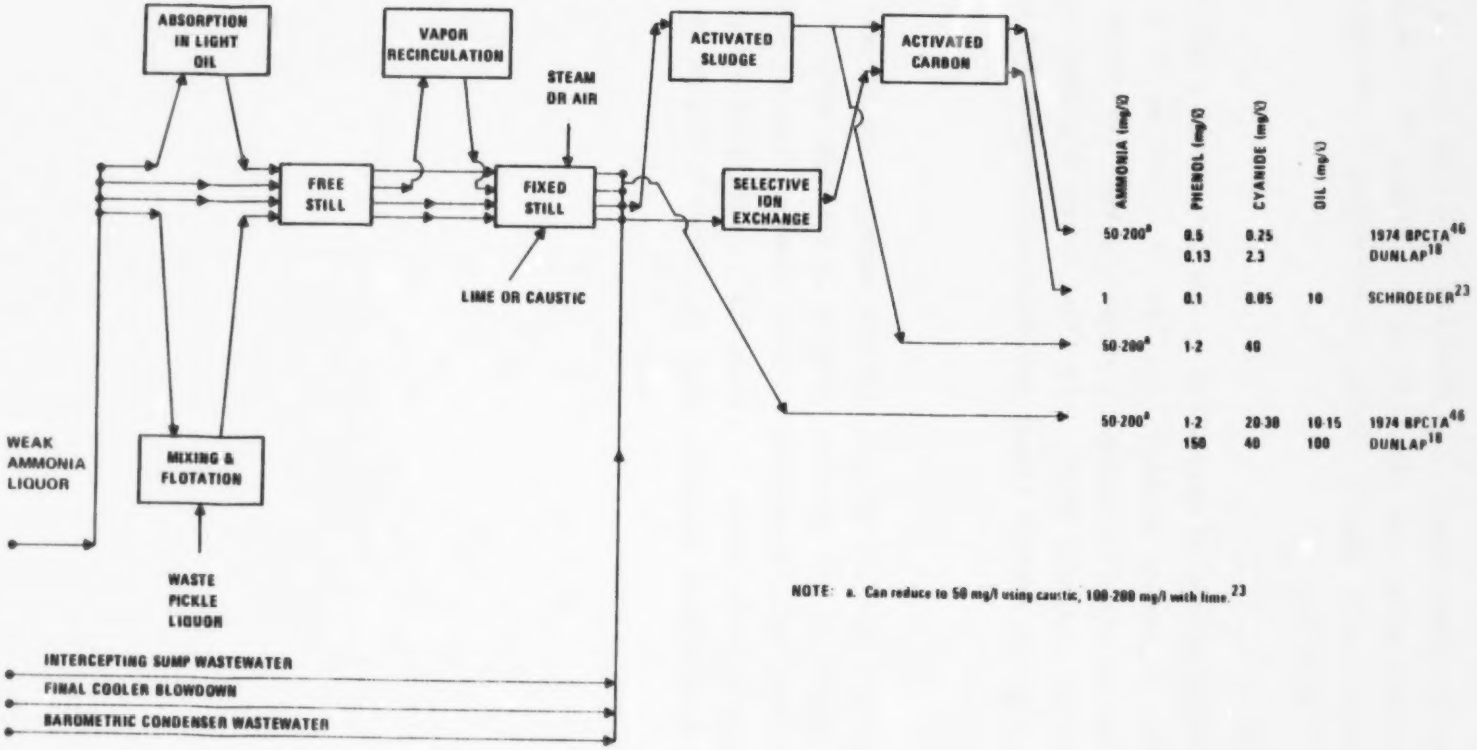
required to keep the reboilers clean. One firm has published plans to put their light oil separator water into the final cooler makeup.[53] This wastewater can also be blended with ammonia liquor, then treated at the plant wastewater treatment facility.

Final Cooler Blowdown

Another significant source of wastewater in the by-product plant is the final cooler blowdown, necessary to control buildup of chlorides in the cooling water. A tightly recycled system is needed to keep the volume of this waste to the lowest possible level. The final cooler blowdown is generally combined with the ammonia liquor and other wastewaters for a one step treatment.

Treatment Options

Wastewater treatment options abound, and the methods tend to overlap and interact with respect to the results. Figure 13 outlines many of the more or less traditional options and their effectiveness. Another approach[23] which has been tested at pilot scale is a completely integrated wastewater treatment scenario developed by Republic Steel and shown in Figure 14.


ABSORPTION IN LIGHT OIL
VAPOR RECIRCULATION
STEAM OR AIR
ACTIVATED SLUDGE
ACTIVATED CARBON
FREE STILL
FIXED STILL
SELECTIVE ION EXCHANGE
LIME OR CAUSTIC
WEAK AMMONIA LIQUOR
MIXING & FLOTATION
WASTE PICKLE LIQUOR
INTERCEPTING SUMP WASTEWATER
FINAL COOLER BLOWDOWN
BAROMETRIC CONDENSER WASTEWATER
AMMONIA (mg/l)
PHENOL (mg/l)
CYANIDE (mg/l)
OIL (mg/l)
50-200a 0.5 0.25 1974 BPCTA46
0.13 2.3 DUNLAP18
1 0.1 0.05 10 SCHROEDER23
50-200a 1-2 40
50-200a 1-2 20-30 10-15 1974 BPCTA46
150 40 100 DUNLAP18

NOTE: a. Can reduce to 50 mg/l using caustic, 100-200 mg/l with lime.[23]

Figure 13. Coke by-product plant wastewater treatment options.

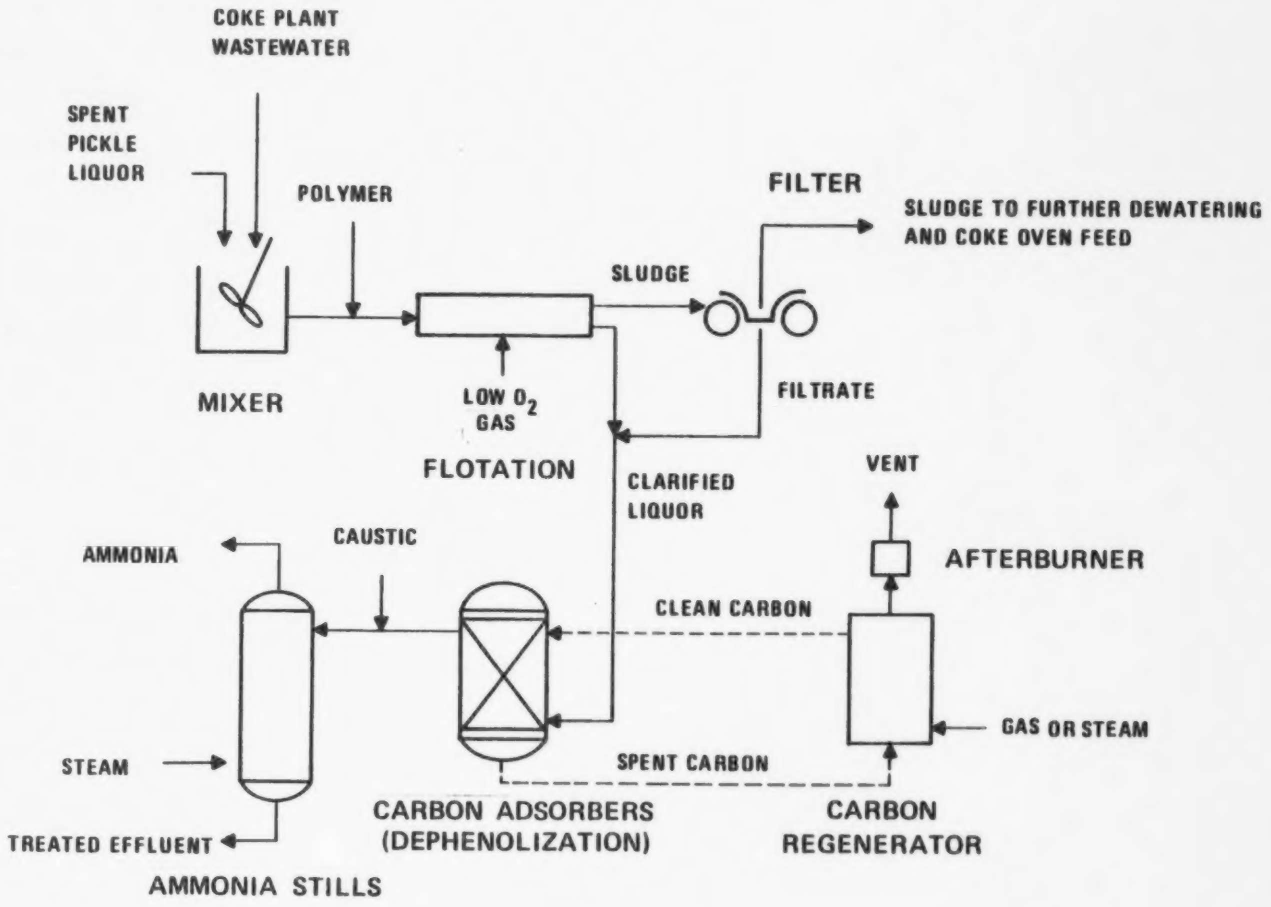

COKE PLANT WASTEWATER
SPENT PICKLE LIQUOR
POLYMER
MIXER
LOW O_2 GAS
FLOTATION
SLUDGE
FILTER
SLUDGE TO FURTHER DEWATERING AND COKE OVEN FEED
FILTRATE
CLARIFIED LIQUOR
VENT
AFTERBURNER
CLEAN CARBON
GAS OR STEAM
SPENT CARBON
CARBON REGENERATOR
CARBON ADSORBERS (DEPHENOLIZATION)
CAUSTIC
AMMONIA
STEAM
TREATED EFFLUENT
AMMONIA STILLS

Figure 14. Complete wastewater treatment scenario.[23]

5.0 STATUS OF BY-PRODUCT RECOVERY TECHNOLOGY IN THE UNITED STATES

5.1 INTRODUCTION

Slightly more than half the by-product coke plants in operation today began coke production prior to 1930. Construction was apparently deferred through the 30's, with new plants again being built in the early 40's and 50's. Only a few plants have started production in the 60's and 70's. The point of this is that many by-product plants were built when coal was the primary source of many important chemicals and by-product recovery was a profitable business. Today, chemicals from petroleum are available in large volumes, at relatively low prices, and with high purity. Chemicals from coal make up a much smaller share of the market and the prices are controlled by the petroleum based chemicals. Coal chemicals were becoming progressively less competitive through the 1960's, and by-product plant operators were losing money on ammonia, for instance.[26] Existing facilities for tar refining and light oil refining were sometimes decommissioned, sometimes not repaired, as small-scale refining wasn't profitable. Today, with the price of all energy sources rising, the economic situation with respect to by-product plants is not clear, but has improved somewhat.

The precise status of by-product plant technology was not determined during this study and is not directly available in the literature. It is possible to get a reasonable picture of the major processing technologies in use today from the 1977 AISI Directory.[54] Table 11 presents a summary of the information obtained from the directory. It should be pointed out that Table 8 rests heavily on the assumptions listed in the notes, and there are almost sure to be some inaccuracies, particularly with regard to the processing of excess ammonia liquor and the final cooler/naphthalene processing routes. The AISI directory lists those coke plants associated directly with the steel industry, providing a short list of products and an abbreviated list of processes for each plant. Those coke plants not listed are generally smaller plants, the omissions being the plants of Allied Chemical Com-

TABLE 11. USE OF COKE BY-PRODUCT RECOVERY TECHNOLOGIES IN THE UNITED STATES

PLANTS	Number of Ovens	TAR			PRIMARY COOLER		AMMONIA HANDLING				FINAL COOLER				LIGHT OIL		SULFUR		COMMENTS
		Crude Tar Handling[a]	Tar Refining On-site	Tar Burned as Fuel[b]	Direct	Indirect	Absorption – to sulfate	Absorption – to phosphate	Other Processes[c]	Dephenolization	Direct Contact Water Type	Tar Bottom Water Contact[d]	Other – i.e., Wash Oil	Naphthalene Handling[e]	Light Oil Recovery	On-site Refining[f]	Desulfurization	Source of Data[g]	
Alan Wood Steel Company, Swedeland, PA	110	X				X	X		?			X			X	X			Status of Company Uncertain
Armco – Houston Works, TX	62	X				X	NI	NI	?		NI	NI	NI	NI	NI	NI			Koppers Benzol Plant; Coke Oven Gas Incinerated
Armco – Middleton, OH	190	X			X		X			X			?		X	X	Dravo/Still		Wilputte Benzol; Phosam Process
Armco – Hamilton, OH	110	X			X		X				X			X	X				
Bethlehem – Bethlehem, PA	364	X			X		X				X			X	X	X	Sulfiban	55	Otto Benzene Plant, Claus Sulfur
Bethlehem – Sparrows Point, MD	751	X			X		X				X	?	?	X	X	X	X	55	Koppers Benzene Plant, Claus Sulfur
Bethlehem – Lackawanna, NY	494	X			X		X			X	X			X	X	X	X		Otto Benzene Plant
Bethlehem – Johnstown, PA	315	X	X		X		X					X			X	X	X	55	Koppers Benzene Plant
Bethlehem – Burns Harbor, ID	164	X			X		X						X		NI		VC	55,51	
C, F & I – Pueblo, CO	143	X	X			X	X					X	X		X	X		55,53	
Crucible, Inc. – Midland, PA	113	X				X	X			X		X			X				
Cyclops Corp. – Portsmouth, OH	70	X			X		X		?			X			X				
Ford Motor Co. – Dearborn, MI	205	X			X			X				X			X				
Inland Steel – E. Chicago, ID	502	X	?		X		X			?		X			X		VC?	55,51	Also Produce Pyridine
Interlake, Inc. – S. Chicago, IL	100	X	?		X		X					X			X				Tar Distillation Available – Use Uncertain
Interlake, Inc. – Erie, PA	58	X				X	NI	NI	NI			X			NI	NI			Koppers Benzene Plant; Only Tar Produced
Interlake, Inc. – Toledo, OH	57	X				X	X				X			X	X	X			Koppers Benzene Plant
International Harvester – S. Chicago, IL	45	X			NI	NI	X					X			X				
Jim Walter Resources – N. Birmingham, AL	240	X	X		X		X				NI	NI	NI	NI	X				Semet-Solvey & Koppers Benzene Plant(s)
Jones & Laughlin – Aliquippa, PA	327	X				X	X			X		X			X	X			Koppers Benzene Plant & Badger Hydrofiner Plant
Jones & Laughlin – Pittsburgh, PA	315	X			X	X	X			X		X			X			55	Produces Tar Acids
Kaiser Steel – Fontana, CA	315	X			X		X	X				X			X				
Lone Star Steel – Lone Star, TX	78	X			X		X					X			X	X			
National, Great Lakes – River Rouge, MI	233	X			X		X				X			X	X				
National, Weirton – Weirton, WV	336	X		X	X				X			X			X		VC	56	Ammonia Destruction

See footnotes and legend at end of table.

TABLE 11 (continued)

PLANTS	Number of Ovens	TAR			PRIMARY COOLER		AMMONIA HANDLING				FINAL COOLER				LIGHT OIL		SULFUR		COMMENTS
		Crude Tar Handling[a]	Tar Refining On-site	Tar Burned as Fuel[b]	Direct	Indirect	Absorption – to sulfate	Absorption – to phosphate	Other Processes[c]	Dephenolization	Direct Contact Water Type	Tar Bottom Water Contact[d]	Other – i.e., Wash Oil	Naphthalene Handling[e]	Light Oil Recovery	On-site Refining[f]	Desulfurization	Source of Data[g]	
National, Granite City – Granite City, IL	137	X				X	X		?			X			X				
Republic Steel – Youngstown, OH	162	X				X	X				X			X	X	X			
Republic Steel – Warren, OH	80	X				X	X					X			X				
Republic Steel – Massillon, OH	31	X			X		X					X			X				
Republic Steel – Cleveland, OH	330	X				X	X			X		X			X			55	
Republic Steel – S. Chicago, IL	75	X				X	X			X	?	X			X			55	
Republic Steel – Gadsden, AL	130	X			X	X	X				X			X	X	X		55	Produce Solvent Naphtha & Naphthalene
Republic Steel – Birmingham, AL	65	X			X		X					X			X				
Sharon Steel – Fairmont, WV	60	X				X	X					X			X	X			
Shenango, Inc., – Neville Island, PA	105	X			X		X					X			X				
U.S. Steel Corp. – Clairton, PA	1,314	X	X		NI	NI			X	X	NI	NI	NI	NI	X	X	Carbonate Claus SCOT	–	Handles Some Chemicals From Other USS Plants
U.S. Steel Corp. – Fairless Hills, PA	174	X			X		X			X	X			X	X				Wide Range of Processing Facilities
U.S. Steel Corp. – Lorain, OH	413	X				X	X					X			X				Wilputte Vacuum $(NH_4)_2SO_4$ Crystallization
U.S. Steel Corp. – Duluth, MN	115	X				X	X					X			NI	NI			
U.S. Steel Corp. – Gary, ID	584	X	X		X		X				NI	NI	NI	NI	X	X		55	
U.S. Steel Corp. – Geneva, UT	252	X			X				X		X			X	X	X			Anhydrous NH_3 Plant
U.S. Steel Corp. – Fairfield, AL	489	X	X			X	X			X	X			X	X			55	
Wheeling-Pittsburgh – E. Steubenville, WV	224	X				X	X					X			X				
Wheeling-Pittsburgh – Monessen, PA	93	X			X		X			X		X			X				Koppers Benzene Plant
Youngstown S & T – Campbell, OH	228	X			X		X					X			X				Semet-Solvay Plant
Youngstown S & T – E. Chicago, ID	237	X			X				X	X		X			X				Sell Ammonia Liquor, No Sulfate

LEGEND

VC : Vacuum Carbonate Desulfurization
NI : No information sufficient to make a decision.
? : Reason for question; lack of conclusive data.

NOTES

[a] Assumed true for all byproduct plants.
[b] Assumed true if tar not listed among byproducts.
[c] Includes Phosam, Anhydrous ammonia processes, Ammonia destruction, etc.
[d] Tar bottom final cooler assumed if naphthalene not listed among byproducts.
[e] Assumed if naphthalene listed among products unless tar refining practiced.
[f] Assumed if light oil products, i.e, Benzene, toluene, xylene, etc., listed separately.
[g] Sources other than 1977 AISI Directory, Reference 54 & 1974 AISI Directory, Reference 22.

pany, Koppers Company, Donner-Hanna Coke Corporation, Alabama By-products Company, and several small gas and chemical producers. The information developed in Table 11 is discussed more fully in the following sections.

Information presented concerning the economics of by-product recovery processes was developed by Wilputte Corporation by factoring and escalating designs which had been developed for their customers. All costs are based on the third quarter of 1977. Details are presented in Appendix B.

5.2 TAR PROCESSING

Coal tar production is unavoidable, and all by-product plants have to deal with it. The tar is initially contained in flushing liquor or a condensed water phase and is physically separated from the aqueous phase in decanters. Emulsion breakers may or may not be used.

Dewatering of tar beyond decantation is described in the literature, but no information as to frequency of use is available. Two types of dewatering equipment could be used: (1) mechanical, such as centrifuges, or (2) heating to elevated temperatures to drive off the water. The use of dewatering equipment depends on the requirements of the tar end-use.

Tar storage may be at elevated temperatures (80° C) to facilitate handling this moderately viscous material. The storage vessels are used for additional decanting at some plants.

The large number of useful chemicals contained in coal tar were once recovered profitably by refining. Table 11 indicates that only six to eight coke plants still have tar refining equipment and it is likely that not all the tar plants listed are operated. According to a Bureau of Mines report,[1] the disposition of crude coal tar in 1975 was roughly 25 percent refined in some degree by the four to eight plants, 25 percent burned by the producer, and the remainder sold to tar distillers.

Coal tar as fuel has risen in favor as the price of fuel has increased. It is possible to burn "cut-back pitch" (tar refining residue diluted with crude tar) as a replacement for Bunker C fuel oil, and it is probable that some tar refiners burn a portion of their tar in this way.

Tar refining can range from simple "topping" to fairly elaborate distillation equipment and sulfur removal capability. Clairton Works of US Steel appears to have the most elaborate tar processing plant among the plants listed by the AISI, producing pitch, pitch-tar mixtures, creosotes, desulfurized naphthalene, and tar acids. Gary Works of US Steel also apparently makes more than one distillate from tar. The other plants included in Table 8 are thought to practice only "topping," a single stage distillation separating pitch and chemical (creosote) oil.

5.3 AMMONIA HANDLING

Most U.S. by-product plants operate in a semi-direct mode with respect to ammonia; that is, the ammonia is distributed between the flushing liquor and the coke oven gas stream. A couple of plants scrub the coke oven gas with water to remove the remaining ammonia and thus put all the ammonia into the liquor; the product of this (indirect) process is aqueous ammonia.

The majority of plants using the semi-direct process must decide what to do with the ammonia in the gas and that in the liquor. Three alternatives are used to treat the liquor: no treatment, free still ammonia stripping, and free and fixed still ammonia stripping. Based on a recent EPA survey[55] of the by-product coking industry, all three alternatives are in use. Out of the 52 plants 33 (63 percent) utilized or were planning both free and fixed stills, four of the plants (8 percent) utilized only free stills, and the remainder apparently did not attempt to recover ammonia from excess ammonia liquor. Once stripped from the liquor, the ammonia is generally routed to the coke oven gas for recovery. Ammonia destruction by incineration is practiced in a few plants. Recovery of ammonia from the coke oven gas is practiced in all the plants that burn coke oven gas as fuel. Only Armco, Houston, is known to incinerate coke oven gas. As shown in Table 11, the majority of plants recover ammonia in some type of scrubber, producing ammonium sulfate in most cases (87 percent) and a phosphate salt in others (4 percent). One plant incinerated its entire ammonia stream. Clairton Works of US Steel produces anhydrous ammonia, utilizing the Phosam® process, and the Geneva Works of US Steel apparently has an ammonium nitrate fertilizer plant on-site.

As shown by the cost estimates presented in Appendix B, ammonia recovery plants are not moneymakers. Ammonia stills to remove ammonia from excess ammonia liquor (6 g/l to 0.015 g/l) have a total operating cost of around \$0.23/100 l of ammonia liquor (\$383 per 1,000 kg of recovered ammonia).

An ammonium sulfate recovery unit operates at a net loss of about $140 per 1,000 kg of ammonia recovered as ammonium sulfate. An existing plant which could be considered fully depreciated, eliminating capital charges, would just about break even.

A Phosam® type anhydrous ammonia plant loses nearly $160 per 1,000 kg of recovered ammonia when capital charges are included.

Of course, the ammonia needs to be removed as a gas purification step, so ammonia recovery of some type is a necessary cost.

5.4 PHENOL RECOVERY FROM AMMONIA LIQUOR

Phenol recovery at by-product plants is uneconomical, and must be looked on as a step in the wastewater treatment. As is shown in more detail in Appendix B, straightforward biological treatment of ammonia liquor for phenol removal is a bit less expensive than building and operating a light oil phenol recovery system, and does a better job of removing phenol. If the dephenolization equipment is in place, operating it is not as expensive as the biological treatment, although some form of additional treatment will be required. About 25 percent of the existing by-product plants use traditional phenol recovery,[55] generally as sodium phenolate. Light oil absorption is apparently a more popular process than vapor recirculation, perhaps due to the tar acids removal effected in a light oil absorber.

5.5 FINAL COOLER AND NAPHTHALENE RECOVERY

Three forms of final cooler and naphthalene recovery technology are in use:

(1) cooling with water and naphthalene recovery by physical separation; or

(2) cooling with water and naphthalene recovery into tar in a tar bottom final cooler; or

(3) cooling with a wash oil which also absorbs naphthalene.

The data in Table 11, above, indicate that about 25 percent of the plants utilize direct water cooling and physical naphthalene recovery, 60 percent utilize tar bottom final coolers, a couple of plants utilize wash oil cooling, and technology at the other plants is not available. The assumptions used in developing Table 11 tend to put uncertain choices in the tar bottom category, however, and thus these numbers should be considered only rough estimates. No information was located concerning the frequency of use of recirculated versus once-through water in the contact final cooler.

The status of naphthalene handling technology after physical separation is not known. The water in the slurry must be decanted or otherwise removed before the naphthalene can be shipped, so some additional handling is needed if water contacts the naphthalene. One variation[55] is to dissolve the naphthalene in coal tar after physical separation.

The choice of final cooler type will have a significant impact on the distribution of some pollutants in a by-product plant, cyanide being a good example. If the cyanide is not removed in the final cooler water, it remains in the gas and causes problems downstream. If it is not stripped out of recirculating cooling water, the blowdown will be high in cyanide and the wastewater plant will be more heavily loaded.

5.6 LIGHT OIL RECOVERY

With few exceptions, light oil is recovered from coke oven gas by wash oil absorption in the United States. Light oil refining capability is present at about 35 percent of the plants listed in Table 11, mostly, but not exclusively, at larger plants. As many of the by-product plants not listed in Table 11 are associated with chemical companies, the fraction refining light oil may well be higher in that group. The products of the refining operations are mostly benzene, toluene, xylene, and solvent naphtha. No data are available to indicate the prevalence of desulfurization of the light oil, although desulfurization is necessary if the light oil products are to compete in the marketplace.

5.7 DESULFURIZATION TECHNOLOGY

The existing U.S. coke oven gas desulfurization plants have been listed in Table 12. No desulfurization technology has proven clearly superior, and all the options appear to be under consideration. Massey and Dunlap[29,32] have presented net amortized capital and operating costs for vacuum carbonate, Sulfiban, Firma Carl Still, and Stretford (with effluent treatment) desulfurization. The Stretford process was the least expensive ($0.0557/Mscf gas) of the high efficiency processes (vacuum carbonate-$0.0717, Sulfiban $0.0825/Mscf),

TABLE 12. COKE OVEN GAS DESULFURIZATION PLANTS IN THE UNITED STATES[32 54 55]

Plant	H_2S Removal From Coke Oven Gas	Sulfur Recovery
Armco Steel, Middletown Coke Plant	Firma Carl Still/Dravo	Sulfuric Acid
Bethlehem Steel Company		
Bethlehem, PA	Sulfiban	Claus Plant
Sparrows Point, MD	Vacuum Carbonate	Claus Plant
*Johnstown, PA	Vacuum Carbonate	
*Lackawanna, N.Y.	Vacuum Carbonate	Claus Plant
Burns Harbor, ID	Vacuum Carbonate	Claus Plant
Donner Hanna Coke Corp., Buffalo, N.Y.	Vacuum Carbonate	
Inland Steel Co., Indiana Harbor, ID	Vacuum Carbonate	Claus Plant
J & L, Pittsburgh, PA	Sulfiban	Claus Plant
National Steel, Weirton, WV	Vacuum Carbonate	Claus Plant
Shenango, Inc., Pittsburgh, PA	Sulfiban	Claus Plant
U.S. Steel, Clairton, PA	Vacuum Carbonate	Claus Plant
Wheeling-Pittsburgh Steel, Follansbee, WV	Firma Carl Still/Dravo	Sulfuric Acid

*May switch to Sulfiban.[57]

but it is also the system with the most limited experience in the United States. For the same degree of removal (99 percent) and plant size, Sulfiban was estimated to be more expensive than vacuum carbonate systems by $0.01 per 1,000 scf of coke oven gas. At the lower efficiency levels (90-93 percent) Sulfiban, Firma Carl Still, and vacuum carbonate were all about the same in cost. Economics of scale were found to be important with costs per volume of gas being $0.02-$0.03/Mscf gas less for 60,000,000 scfd plants than for 20,000,000 scfd plants. Sulfuric acid production costs $0.005 to $0.015/Mscf more than Claus plant sulfur production. High efficiency desulfurization (99 percent) costs around \$0.02/Mscf more than does low efficiency (90-93 percent).

The estimates by Massey and Dunlop do not include by-product credits. Most plants recover the sulfur in a Claus plant, although some of the newer plants recover sulfuric acid. A three- to four-year payout for sulfuric acid plants was estimated in 1975 for acid prices of around \$40/ton. Discounting inflation, acid prices were at about that level in the third quarter of 1977, so acid recovery might be a reasonable investment.

5.8 STATUS OF WASTEWATER TREATMENT

The available data on the status of wastewater treatment are presented in Table 13. As has been described in earlier sections, excess (waste) ammonia liquor is usually partially treated separately, then combined with the other wastewater streams for final treatment and disposition. About 70 percent of the plants utilize ammonia stills and 25 percent dephenolize ammonia liquor. Wastewater treatment scenarios from this point in the flow plan are diverse. Thirteen plants use or plan biological oxidation as part of their treatment scheme; four use or plan chemical oxidation.

As to the ultimate disposition of the wastewater:

- 14 plants (27 percent) discharge to receiving waters following the by-product plant wastewater treatment;
- 11 plants (21 percent) discharge to public treatment facilities;
- 14 plants (27 percent) use part of the coke plant wastewater as quench make-up and discharge the remainder to receiving waters (9 plants), public facilities (3 plants), central treatment (1 plant), or deepwell injection (1 plant);
- 9 plants (17 percent) quench by-product plant wastewater to extinction;
- the remaining 4 plants utilize incineration, reuse, central treatment, and impoundment.

Tight control of the amount of water blowdown is another way to reduce wastewater loadings. Dunlop and McMichael[18] have estimated that plants with tight recycle systems discharge a total of about 480 l/Mg coke (115 gal/ton coke) and that loose recycle systems discharge 1200 l/Mg coke (290 gal/ton). Table 13 indicates that 6 plants recycle barometric condenser water from vacuum crystallizers; unfortunately, the number of vacuum crystallizers was

TABLE 13. STATUS OF BY-PRODUCT PLANT WASTEWATER TREATMENT PROCESSES

	Coke Production Mg/day (tons/day) Typical	USE OF PARTICULAR PROCESS COMPONENTS[1]							Byproduct Plant Waters Used For Quench (Note 2)	Process Outfall Flows l/Mg (gal/ton) Typical	Additional Data–l/Mg (gal/ton) And Comments
		Carbon Treatment	Free Still	Fixed Still	Dephenolization	Bio-Oxidation	Chemical Oxidation	Recycle Baro. Cond. Water			
1. Alabama Byproducts – Tarrant, AL	1,945 (2,140)		N	N		F			FC	629 (151)	
2. Alan Wood – Conshohocken, PA	1,114 (1,225)		N			OS	OS			366 (88)	
3. Armco – Middletown, OH	1,285 (1,414)		N	N	N					237 (57)	To POT
4. Armco – Hamilton, OH	1,646 (1,811)		N	N	N	F				271 (65)	
5. Armco – Houston, TX	763 (840)									none	Incinerated
6. Bethlehem, – Bethlehem, PA	4,599 (5,059)			F		N				495 , (119)	
7. Bethlehem – Sparrows Point, MD	8,330 (9,163)			F		F				unknown	
8. Bethlehem – Lackawanna, NY	6,280 (6,908)		N	N	N			N	FC, BC	unknown	
9. Bethlehem – Johnstown, PA	3,660 (4,026)		N	F		F			EAL, BzP, FC	none	To quench
10. Bethlehem – Chesterton, IN	4,708 (5,179)							N	FC, BC, DS	none	179 (43) deepwell injection
11. Citz. Gas & Coke – Indianapolis, IN	911 (1,002)									1,066 (256)	To POT after settling & skimming
12. Cyclops – Portsmouth, OH	1,041 (1,145)								EAL	391 (94)	Plus 982 (236) to quench
13. Donner Hanna – Buffalo, NY	1,500 (1,650)		N	N	N					216 (52)	Process. 19,185 (4,608) total
14. Philadelphia Coke – Philadelphia, PA	800 (880)		N	N					FC	333 (80)	To POT
15. Ford Motor – Dearborn, MI	3,586 (3,945)		N	N						1,678 (403)	To POT
16. Missouri Coke & Chem. – St. Louis, MO	727 (800)		N							unknown	
17. Inland Steel – E. Chicago, IN	6,547 (7,202)		N	N	N				BzP, FC	299 (72)	To POT
18. Interlake – Chicago, IL	1,327 (1,460)						N			2,873 (690)	To POT
19. Interlake – Toledo, OH	638 (702)									5,808 (1,395)	To POT, no pretreatment
20. International Harv. – Chicago, IL	636 (700)									1,516 (364)	To POT, no pretreatment
21. J & L – Aliquippa, PA	4,094 (4,504)		N	N					EAL, BzP, FC	658 (158)	
22. J & L – Pittsburgh, PA	4,754 (5,230)		N	N	N					400 (96)	
23. Kaiser – Fontana, CA	3,454 (3,800)		N	N	N			N	EAL, BzP, FC	none	137 (33) to quench
24. Koppers – St. Paul, MN	454 (500)		N							3,414 (800)	To POT
25. Koppers – Erie, PA	545 (600)				N		N			137 (33)	To POT
26. Koppers – Bessemer, AL	1,156 (1,272)		N	N		F			FC	982 (236)	
27. Lone Star – Lone Star, TX	627 (690)		N	N						1,869 (449)	Reused
28. National, Great Lakes – River Rouge, MI	4,727 (5,200)		N	N	N					none	All to quench
29. National – Granite City, IL	1,584 (1,743)		N	N					EAL, FC	none	179 (43) to quench
30. National – Weirton, WV	7,075 (7,783)		N	N		N	F		BzP, FC	572 (137)	
31. Milwaukee Solvay – Milwaukee, WI	536 (590)									566 (136)	To POT, no pretreatment

See footnotes at end of Table.

TABLE 13 (continued)

	Coke Production Mg/day (tons/day) Typical	USE OF PARTICULAR PROCESS COMPONENTS[a]							Byproduct Plant Waters Used For Quench (Note b)	Process Outfall Flows l/Mg (gal/ton) Typical	Additional Data– l/Mg (gal/ton) And Comments
		Carbon Treatment	Free Still	Fixed Still	Dephenolization	Bio-Oxidation	Chemical Oxidation	Recycle Baro. Cond. Water			
32. Republic – Youngstown, OH	2,486 (2,735)								EAL, BzP, FC	none	341 (82) to quench
33. Republic – Warren, OH	1,163 (1,279)		N	N					EAL, BzP, FC	604 (145)	Plus 474 (114) to quench
34. Republic – Massilon, OH	454 (500)		N	N						none	999 (240) impoundment
35. Republic – Cleveland, OH	4,676 (5,144)	F	N	N	N				BzP	596 (143)	Process
36. Republic – Chicago, IL	1,182 (1,300)		N	N	N					96 (23)	To POT
37. Republic – Gadsden, AL	1,623 (1,785)		N	N		N		N		908 (218)	To central treatment
38. Republic – Birmingham, AL	509 (560)		N	N						2,899 (694)	
39. Sharon Steel – Fairmont, WV	509 (560)		N	N	N					1,932 (464)	
40. Shenango – Neville Island, PA	1,782 (1,960)	F	N	F	N		F		FC	458 (110)	Process. 17,572 (4,220) total flow
41. Jim Walter – N. Birmingham, AL	2,182 (2,400)		N	N		N				1,736 (417)	Includes dilution
42. US Steel – Clairton, PA	18,545 (20,400)		N	N	N	N				512 (123)	Process. 942 (226) total flow
43. US Steel – Fairless Hills, PA	2,727 (3,000)		N	N	N	N		N	FC, BC	179 (43)	To central treatment
44. US Steel – Lorain, OH	3,926 (4,319)							N	EAL, BzP, BC	none	258 (62) as quench
45. US Steel – Duluth, MN	1,147 (1,262)		F							1,948 (468)	
46. US Steel – Gary, IN	8,864 (9,750)								EAL, FC	79 (19)	To POT + 682 (164) as quench
47. US Steel – Geneva, UT	3,200 (3,520)		N	N					EAL, BzP, FC	none	532 (128) as quench
48. US Steel – Fairfield, AL	4,495 (4,945)		N	N	N	N				849 (204)	
49. Wheeling Pitt. – Monessen, PA	1,211 (1,332)		N	N	N					204 (49)	Process. 3,626 (871) total flow
50. Wheeling Pitt. – Follansbee, WV	3,539 (3,893)		N	N	N	F				208 (50)	
51. YS&T – Campbell, OH	3,166 (3,483)		N	N					EAL, BzP, FC	none	258 (62) as quench
52. YS&T – E. Chicago, IN	3,096 (3,406)		N	N	N					379 (91)	To POT

NOTES:

a. N = now in use, F = future, OS = out of service.

b. FC = final cooler, EAL = excess ammonia liquor, BzP = benzene plant, BC = barometric condenser water, DS = desulfurizer.

POT = publicly owned treatment.

not determined by the survey. Effluent flows given in Table 13 range from about 80 to 5,800 l/Mg coke. The low end of this reflects use of wastewater for quenching and the high end presumably includes some once-through cooling water.

Disregarding plants with effluent rates above 2,500 l/Mg coke (to eliminate large-scale once-through cooling water use) and those that wastewater quench leaves us with effluent rates between 96 and 1,932 l/Mg coke (23-468 gal/ton), with an average of 838 l/Mg coke.

6.0 ENVIRONMENTAL EFFECTS OF COKE BY-PRODUCT RECOVERY

6.1 SUMMARY

The purpose of a Level 1 environmental assessment is to provide a screening or survey look at emissions from an industry, highlighting potential problem areas for further work if justified.[58] Within these limits, the environmental effects of a by-product coke plant are assessed in this Section. The test work was done at the Fairfield Works of U.S. Steel Corporation, near Birmingham, Alabama. Other information was available in the literature and is presented when appropriate.

The Level 1 assessment protocol recommends that all identified emissions to all media be sampled and analyzed, as well as the feeds to and products from the process. All of the samples are grab samples, and the intended accuracy is to be within a factor of 2 or 3 of the actual emissions. Procedures and equipment are specified for a Level 1 assessment; these are discussed in detail in Appendix A.

Examination of the process flow of a by-product plant showed that most air emissions were fugitive, and primarily composed of organic compounds. The potential for these fugitive emissions to contain significant amounts of aromatics and high molecular weight polynuclear aromatics (PNA's) was apparent, and was important in the development of the analysis program. Hydrogen cyanide was also identified as a potentially significant component.

Liquid by-product plant wastes were and are presently a subject of detailed study by the Effluent Guidelines Division of EPA. The analyses done by the Effluent Guidelines Division were more extensive than possible with the Level 1 methods used in this project. Their sampling was also being done at Fairfield Works and in view of this fact, liquid sampling was limited in this study. The Effluent Guidelines data have been included in this report. The literature indicated a single major solid waste, the biological plant sludge, which was sampled.

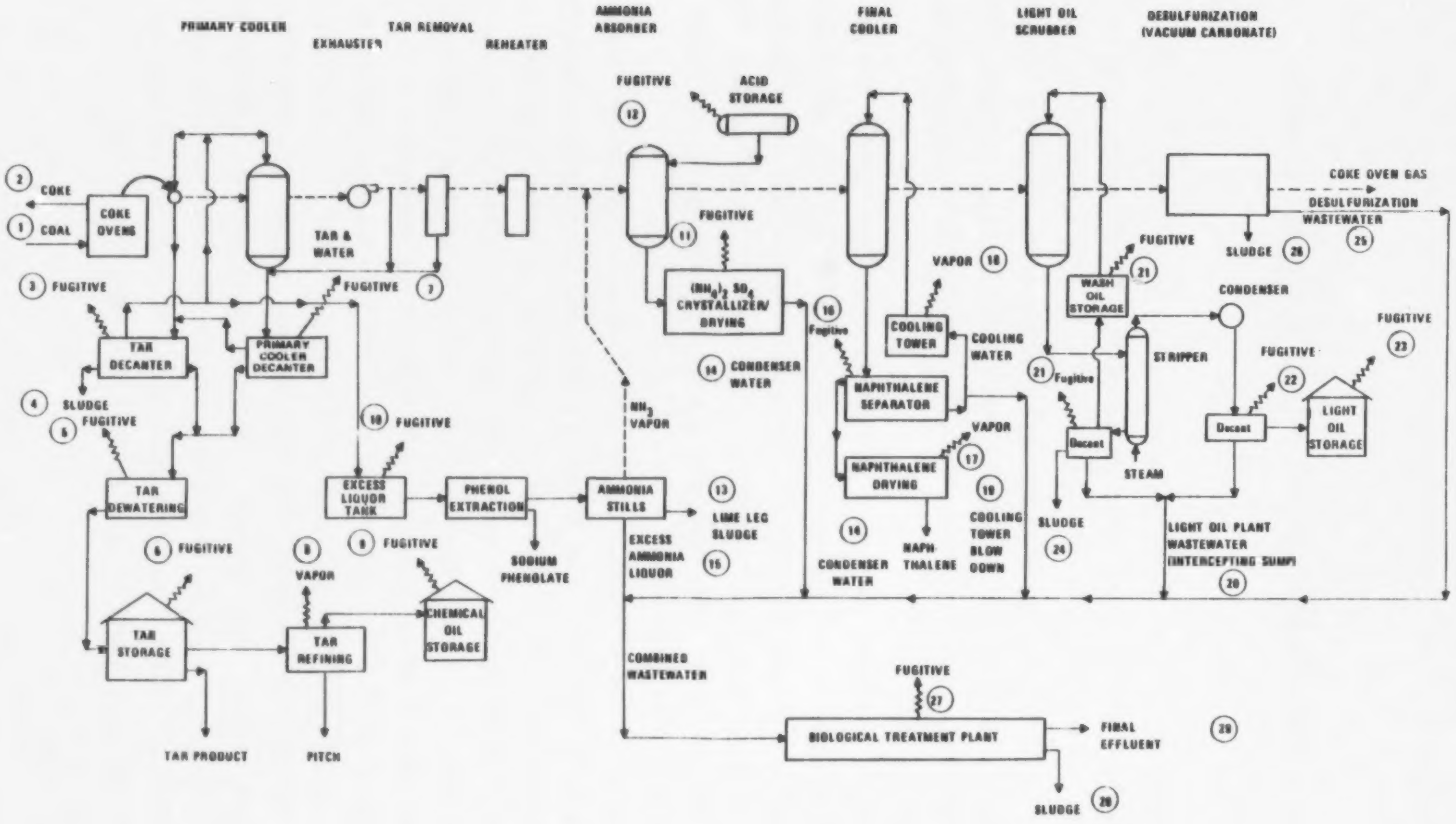

PRIMARY COOLER
EXHAUSTER
TAR REMOVAL
REHEATER
AMMONIA ABSORBER
FINAL COOLER
LIGHT OIL SCRUBBER
DESULFURIZATION (VACUUM CARBONATE)
2 COKE
1 COAL
COKE OVENS
TAR & WATER
3 FUGITIVE
FUGITIVE 7
TAR DECANTER
PRIMARY COOLER DECANTER
4 SLUDGE
5 FUGITIVE
TAR DEWATERING
6 FUGITIVE
TAR STORAGE
TAR PRODUCT
8 VAPOR
TAR REFINING
PITCH
9 FUGITIVE
CHEMICAL OIL STORAGE
10 FUGITIVE
EXCESS LIQUOR TANK
PHENOL EXTRACTION
SODIUM PHENOLATE
NH3 VAPOR
AMMONIA STILLS
13 LIME LEG SLUDGE
EXCESS AMMONIA LIQUOR 15
COMBINED WASTEWATER
FUGITIVE 12
ACID STORAGE
FUGITIVE 11
(NH4)2 SO4 CRYSTALLIZER/ DRYING
14 CONDENSER WATER
16 Fugitive
NAPHTHALENE SEPARATOR
NAPHTHALENE DRYING
VAPOR 17
14 CONDENSER WATER
NAPH-THALENE
VAPOR 18
COOLING TOWER
COOLING WATER
19 COOLING TOWER BLOW DOWN
21 Fugitive
WASH OIL STORAGE
FUGITIVE 21
Decant
SLUDGE 24
STRIPPER
STEAM
CONDENSER
FUGITIVE 22
Decant
FUGITIVE 23
LIGHT OIL STORAGE
LIGHT OIL PLANT WASTEWATER (INTERCEPTING SUMP) 20
SLUDGE 26
COKE OVEN GAS
DESULFURIZATION WASTEWATER 25
FUGITIVE 27
BIOLOGICAL TREATMENT PLANT
FINAL EFFLUENT 29
SLUDGE 28

Figure 15. Pollutants from by-product recovery.

TABLE 14. POLLUTANTS FROM BY-PRODUCT RECOVERY PLANT

Stream Number	Stream Identification	Rate: Constituents Based on 1 Mg Coke Production
1	Coal	1.4 Mg
2	Coke	1 Mg
3	Tar Decanter-Fugitive	2.15 sm^3/Mg: benzene, 15.6 g/Mg; H_2S 12.7 g/Mg; XAD-2 sample primarily LC cut #2*
4	Tar Sludge	0.1 l/Mg (very rough estimate): contains tar, coal, and coke fines; no Level 1 analysis
5	Tar Dewatering-Fugitive	Included in 6 below
6	Tar Storage-Fugitive	0.14 sm^3/Mg (working loss only): low rate benzene, toluene; XAD-2 sample primarily LC cut #2*
7	Primary Cooler Condensate Fugitive	1.7 sm^3/Mg: benzene, 9 g/Mg coke; H_2S 5.7 g/Mg; XAD-2 sample not collected
8	Tar Refining-Vapor	Not sampled.
9	Chemical Oil Storage-Fugitive	.024 sm^3/Mg (working loss only): low rate benzene, toluene; XAD-2 sample mostly LC cut #2* and #3
10	Excess Liquor Tanks-Fugitive	Not sampled: at lower temperature than 7 above, but roughly same composition
11	Sulfate Drying	Not sampled
12	Acid Storage-Fugitive	No measurable vent: not sampled
13	Lime Leg Sludge	0.35 kg/Mg: primarily calcium salts
14	Barometric Condenser Water	143 l/Mg: cyanide, 2 g/Mg; ammonia, 1.6 g/Mg; phenol, 0.5 g/Mg (Dunlap and McMichael)
15	Excess Ammonia Liquor	143 l/Mg: cyanide, 8.6 g/Mg; ammonia, 857 g/Mg; phenol, 208 g/Mg (Dunlap and McMichael)
16	Naphthalene Separation	No measurable vent rate: vapor high in benzene and homologs, H_2S; XAD-2 sample mostly LC cuts #2* and #3
17	Naphthalene Drying	2.9 sm^3/Mg: Naphthalene emissions as high as 533 g/sm^3, but an average must be considerably lower.
18	Final Cooler Cooling Tower	3,230 sm^3/Mg: benzene, 51.6 g/Mg; H_2S, 11 g/Mg; XAD-2 sample mostly LC cuts #2* and #3
19	Cooling Tower Blowdown	43-430 l/Mg: cyanide, 22-43 g/Mg; ammonia, 8-17 g/Mg; phenol, 10-16 g/Mg (Dunlap and McMichael)
20	Light Oil Plant Wastewater	100-500 l/Mg: cyanide, 0.5-1 g/Mg; ammonia, 0.5-1.5 g/Mg; phenol, 0.8-26 g/Mg (Dunlap and and McMichael); 3 kg/Mg oil (Schroeder)
21	Wash Oil Tanks-Fugitive	No measurable vent: not sampled
22	Light Oil Decanter-Fugitive	Inaccessible: not measured or observed
23	Light Oil Storage-Fugitive	0.013 sm^3/Mg working loss, 15.6 sm^3/Mg breathing loss (crude estimate[95]): benzene, 17.4 g/Mg; toluene, 0.6 g/Mg; H_2S, 0.5 g/Mg
24	Wash Oil Sludge	Not sampled and rate not available.
25	Desulfurization Wastewater	40-60 l/Mg vacuum carbonate plant: cyanide, 64 g/Mg (Dunlap and McMichael)
26	Desulfurization Sludge	Not quantified
27	Wastewater Plant Fugitive	No measurable rate
28	Wastewater Plant Sludge	1.7 kg/Mg: high phenolic levels
29	Final Effluent	470-1,260 l/Mg coke: BPCTCA gives 730 l/Mg; cyanide, 20 g/Mg; ammonia, 91 g/Mg; phenol, 1.5 g/Mg; oil, 11 g/Mg

*LC Cut #2 expected to contain aromatic hydrocarbons, fused polycyclics, fused nonalternant polycyclics, and possibly halogenated aromatics.

The sampling program developed for this study was centered on organic vapor emissions from tank vents and a cooling tower. Appendix A contains a more complete description than that given below. Three types of sampling were used for the organic vapors: (1) glass bulb grab samples, (2) evacuated canister grab samples, and (3) 1 to 4 hour samples drawing the gas through an adsorbant resin, XAD-2. The glass bulbs were analyzed for light (C_1-C_7) hydrocarbons and volatile sulfur species using an on-site gas chromatograph (GC). Benzene and toluene were also quantitated with this GC. The evacuated canister samples were returned to the laboratory for analysis to identify and quantitate benzene, toluene, the xylenes, and ethylbenzene. The adsorbant resin was intented to adsorb hydrocarbons with carbon numbers greater than 7, or boiling points above about 100° C. The resin was extracted with a solvent and the extract analyzed in three ways:

(1) Total Chromatographable Organics (TCO), which is nominally the mass of organic compounds with boiling points between 200° C and 300° C;

(2) Gravimetric Analysis (GRAV), which is nominally the mass of organics with boiling points above 300° C; and

(3) Liquid Chromatography, LC, which is used to divide an extract into seven fractions (or cuts) which are graded by their polarity.

The analysis generally proceeds with a TCO and GRAV analysis of the original sample extract (preliminary), a concentration step to achieve a specified organic concentration (GRAV and TCO are also run on this concentrate), and then the LC work, with a GRAV and TCO determination on each LC cut.

Liquid and solid samples were handled in much the same way, the liquids being extracted with a solvent at pH 2 and at pH 12, the solid sample was extracted at pH 7. This extract was then treated in the same way as the adsorbant resin extracts.

Further analysis of the Level 1 samples included infrared spectroscopy (IR) and low resolution mass spectroscopy (LRMS). Unfortunately, solvent interference prevented the extraction of much useful information from the LRMS, which forced reliance on the IR data for compound identification and rough quantitation, as described later in this summary.

In addition to the Level 1 sampling and analysis, samples for hydrogen cyanide were taken at the final cooler cooling tower and 24-hour integrated samples were collected at three points around the plant boundary. The gas was bubbled through a sodium hydroxide solution for cyanide absorption and analyzed by wet chemistry.

The results of this sampling and analysis are presented in two ways. A generalized, hybrid plant was developed (Figure 15) and used as a basis to present the available data. This hybrid plant is thought to be close to a widely used, relatively complete plant. The emission rates given in Table 14 are based on the sample work done at Fairfield or on the literature. A brief description--amplified later in this Section--is also given for the identified emissions. Excluded from the table are the pump seal leaks, flange leaks, and other similar problems which plague chemical plants. Also not addressed are certain periodic cleaning operations which are necessary for some pieces of equipment. Standard conditions are 20° C and 760 mm Hg throughout this report.

The emissions are discussed further in sections on each emission. The majority of the Level 1 data is presented in these discussions. The presentation of the LC work demands special explanation. These LC separations, with identification supported by IR, were summarized using a modification of the Harris format.[59] All organic compounds were assigned to one of 17 compound classes, these based on categories developed in the Multimedia Environmental Goals (MEG's) publication.[60] These compound classes have chemical properties which lead one, two, or perhaps three of the LC cuts, but not in all cuts.[59] The LC and IR data was summarized as follows:

(1) If any compound class or member of a class was tentatively identified by the IR of an LC cut, it was assumed that that compound class was present in the LC cut in the amount of the GRAV mass (IR's were run only on the GRAV samples, per Level 1).

(2) A compound class which was considered possible in a LC cut, but which was not identified by IR, (but could not be excluded on IR evidence) was assumed to be present in the LC cut in the amount of 10 percent of the GRAV mass of the LC cut.

(3) The values derived in (1) and (2) above were divided by the sample volume and are called MATE comparison values, with concentration

units. The MATE comparison values presented in this chapter have been summed across all the LC cuts to arrive at a total sample MATE comparison value for each compound class.

These MATE comparison values, unlike the pollutant concentrations derived from the GC work, are admittedly synthetic. In most cases the MATE comparison values for a LC cut total more than the GRAV mass from which they were derived. On the other hand, the MATE comparison values cannot be called "maximum possible," as the TCO mass was excluded from consideration. Fortunately, the results of gas chromatograph/mass spectrometer (GC/MS) analysis of three of the samples serves to clarify the situation, identifying those compounds which are actually present.

To assist in the interpretation of the pollutant concentrations (from the GC work) and MATE comparison values (from the LC and IR work), yardsticks are derived from the MEG's charts.[60] For the sake of conservatism, the most toxic compound in each of the 17 compound classes was identified and its Minimum Acute Toxicity Effluent (MATE) concentration was used for comparison (for many compounds for which "Threshold Limit Values," TLV's, have been cited, the MATE concentration is the TLV). The yardstick used was the ratio formed between the MATE comparison value and the lowest MATE concentration for a compound class.

It must be kept in mind that the resulting ratio is biased. If it is well below unity there would appear to be no concern for compounds in this class; if, however, the ratio is above unity, it is merely a signal for more research. Level 1 assessment only illuminates the areas where more research will be profitable. Due to the wide variation in MATE concentrations within a compound class, the verification that one especially toxic compound cannot reasonably be present in the emission could easily carry the ratio from well above to well below unity--from a source of concern to its opposite.

One further comment concerning the organic data is needed. Naphthalene was present in large amounts in many of the organic vapor samples. Indeed, it condensed and plugged the sample train on several occasions. The naphthalene in these very high concentrations to some extent defied both the TCO-GRAV split into heavy and light organics and the LC split by polarity. The aromatic concentrations given, in many cases, are primarily contaminated naphthalene.

The total GRAV and TCO concentrations in the sample are presented, indicating the relative amounts of high boiling (b.p. > 300° C for GRAV) and low boiling compounds. The IR work used on the LC cuts was done entirely on GRAV samples, so only GRAV masses are reflected in the MATE value comparison concentrations.

Three of the samples were further examined by GC/MS, and the actual compounds identified in these samples are listed in a continuation of the organic summary table.

6.2 ENVIRONMENTAL EFFECTS OF COAL TAR COLLECTION AND PROCESSING

The emissions from tar processing are essentially all fugitive in nature. The primary sources are:

- emissions From Tar Decanters
- primary Cooler Condensate Holding Tank
- emissions From Tar Dewatering/Storage
- tar "Topping" Emissions
- tar Distillation Products Storage.

Emissions From Tar Decanters

As has been described, tar decanters are often elongated, multi-compartment, rectangular tanks, the tar collecting on the bottom of the tank and flushing liquor being removed at the top. In addition to these two primary streams, a sludge accumulates in the initial compartment, or may be collected by a drag conveyor from the bottom of the decanter. As the temperature of the flushing liquor in the decanters is around 80° C, vaporous emissions may be visible from the vent pipes of a covered decanter. In addition, open or warped hatches allow additional emissions.

The sludge from a tar decanter was not analyzed. The sumps at the sampled plant were cleaned on the order of once a week (rough estimate 0.1 l of sludge/Mg coke). The sludge consists of coal and coke fines mixed with coal tar and resins. Thus, the full range of tar components is present. Disposal at the plant visited was to an on-site dumping location (unspecified). However, disposal on the coke pile or coal pile for recycle to the ovens should be possible.

Vapor emissions were determined from three tar decanters serving four batteries. The results of the sampling and analysis are presented in Table 15. The overall emission rate from the three decanters was about 2.15 sm^3/Mg coke produced. The emission rate as given is the total emission divided by the production rate at the plant during the sampling week, 3600 Mg coke/day. This is a reasonable first approximation; but the emission rate varied considerably from decanter to decanter, and is probably more dependant on the design and number of decanters than on production.

As can be seen in Table 15, the benzene and hydrogen sulfide concentrations in this source are well above the MATE values, and some possible problem areas were identified by the liquid chromatography work. The GC/MS work presented on the continuation page of Table 15 shows that several of the compound classes possible from the IR are not actually present. Aromatic hydrocarbons as a class remain above the MATE value.

Primary Cooler Condensate Holding Tanks

At the sampled plant the primary cooler condensate holding tanks (which also served to decant additional tar) were tall cylindrical tanks (height to diameter of about 3:1) around 15 feet in diameter. The tanks were vented through short pipes. Gas temperature in the vent was 62° C with a measurable emission. The vent rate was estimated at 1.7 sm^3/Mg coke by extrapolating one measured rate to two other tanks in the same service (assumed same vent rate) for a combined total emission. Emissions from this source are summarized in Table 16. As above, benzene and H_2S are present in concentrations well above the MATE values.

Emission from Tar Dewatering/Storage

The emissions from a separate tar dewatering step were not directly determined during this study. The plant visited utilized heated (80° C) tar storage, the emissions from which should be similar in composition to dewatering by steam heat. Dewatering by centrifuge should result in reduced emissions in comparison to heated tanks, although the overall effect would be lessened if heated tar storage tanks were also used in the same plant.

TABLE 15. SUMMARY OF ORGANIC ANALYSIS, TAR DECANTER VAPOR
Emission rate: 2.15 sm^3/Mg coke

Compounds Identified by GC	Concentration, mg/sm^3	MEGs[a] Category Number	MATE[b] Values, mg/sm^3	Ratio $\left(\frac{\text{Conc. Found}}{\text{MATE}}\right)$
C_1-C_7 HC(Avg. MW≅22)	4,550	1	min. = 32	142
Benzene	7,283	15	3	2,430
Toluene	746	15	375	2.0
Xylenes and ethylbenzene	186	15	435	0.43
Sulfur compounds (as H_2S)	5,914	53	15	394

Liquid Chromatography	MATE Comparison Value, mg/sm^3	MEGs[a] Category Number	Min. MATE[b] Value in Category	Ratio
Aliphatic hydrocarbons	141.8	1[c]	32	4.4[c]
Halogenated aliphatics	3.2	2[c]	0.1	32[c]
Aromatic hydrocarbons	*519*	*15,21A,22*	*1.0*	*519*
Halogenated aromatics	43.0	16[c]	0.7	61.4[c]
Heterocyclic N, O, S compounds	*0.95*	*23,24,25*	*0.1[9]*[d]	*9.5*[c]*[0.1]*[d]
Sulfides, disulfides	0.95	13b	20	0.04[c]
Nitriles	0.95	9[c]	1.1	0.86[c]
Ethers	185	3[c],4[c]	0.01	18,500[c]
Aldehydes, ketones	82.8	7[c]	0.2	414[c]
Nitroaromatics	3.33	17[c]	1.0	3.33[c]
Alcohols	6.4	5[c],6[c]	10	0.64[c]
Amines	8.16	10[c],11[c],12[c]	0.001	8,160[c]
Phenols	*5.9*	*18,19*[c]*,20*[c]	*0.1[10]*[d]	*59*[c]*[0.59]*[d]
Esters, amides	157	8C,8D[c]	1.0	157[c]
Mercaptans	2.95	13A[c]	1.0	2.95[c]
Carboxylic acids	24.2	8A,8B[c]	0.3	81[c]
Sulfoxides	2.96	14[c]	1.0	2.96[c]

GRAV conc. in sampled gas 2,720-3,550 mg/sm^3

TCO conc. in sampled gas 5,110 mg/sm^3

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[a] MEG = Multimedia Environmental Goals

[b] MATE = Minimum Acute Toxicity Effluent

[c] Not indicated by GC/MS work

[d] Reflects compounds found by GC/MS work
Italics highlight categories found by GC/MS.

TABLE 15. (continued)

IDENTIFICATION

Elution Temperature (°C)	Compound	Elution Temperature (°C)	Compound
70	Benzene	161.7	C_2-naphthalene
70	Toulene (?)	162.3	Biphenylene
98.3	Phenol	167.1	Acenaphthene
101.2	Indene	167.7	Methyl-biphenyl
107.9,113.1	Cresols	172.3	Dibenzofuran
118.5	Divinyl benzene (?)[a]	178.3	Methyl-acenaphthene
123.0	Naphthalene	180.3	Fluorene
124.6	Benxothiophene	183.5	Carbazole (?)
131.0	Quinoline or isoquinoline	185.7	Hydroxyfluorene isomer
134.8	Methylindene	186.3	Methylacenaphthene isomer (?)
140.6	Methylnaphthalene	187.9	Hydroxyfluorene isomer
143.5	Methylnaphthalene	201.4	Dibenzothiophene
174.4	Indole	204.6	Phenanthrene
149.2	Methyl-quinoline	205.5	d_{10}-anthracene[b]
153.1	Biphenyl	206.2	Anthracene (?)
156.3	C_2 -naphthalene	220.3	4,5-Methylenephenanthrene
156.9	C_2 -naphthalene	236.3	Fluoranthene
158.8	C_2 -naphthalene	241.7	Pyrene

QUANTITATION

Of those compounds identified, only quinoline and biphenyl were quantitated. Subjectively, naphthalene appeared to be the prevalent compound.

Compound	Wt. of Compound In XAD Extract (mg)	Wt. of Compound in Canister Rinse (mg)	Total Wt.	Concentration (mg/sm^3) in Gas Sample
Biphenyl	144.3	14.9	159.2	19.6
Quinoline	294.2	29.1	323.3	39.7

[a] Often an artifact from sample contact with plastics.

[b] Internal standard.

TABLE 16. SUMMARY OF ORGANIC ANALYSIS, PRIMARY COOLER CONDENSATE TANK VENT

Emission Rate: 1.7 sm^3/Mg coke

Compounds Identified by GC	Concentration mg/sm^3	MEG's Category[a] Number	MATE Value[b] (mg/sm^3)	Ratio $\left(\frac{\text{Found}}{\text{MATE}}\right)$
C_1-C_7 HC (Average MW≅23.6)	1,883	1	min. = 32	59
Benzene	5,230	15	3	1,740
Toluene	649	15	375	1.7
Xylenes and ethylbenzene	215	15	435	0.5
Sulfur compounds (as H_2S)	3,324	53	15	222

[a] MEG = Multi-Media Environmental Goals.

[b] MATE = Minimum Acute Toxicity Effluent.

Emissions from Tar Storage Tanks

Tar is commonly stored in heated tanks in order to facilitate handling. A single tar storage tank was sampled, and the results were extrapolated to all the tar storage tanks. Storage was at approximately 80° C. Naphthalene condensation was evident at all vents and hatches on the tank. The emissions are summarized in Table 17. Again, benzene and the aromatic hydrocarbons class were present in amounts above the MATE values. The emission rate could not be measured, and that given was estimated strictly as working loss. Some problem areas were identified by the LC work.

Two aspects of this estimate deserve special comment. The tar storage tanks at the plant visited were cone roof cylindrical tanks with a vent pipe in the center of the roof. In addition, the tanks were vented by slits roughly 20 cm high spaced around the perimeter of the tank directly below the roof junction. As wind must enter the tank through these vents, emissions from these tanks are probably at a higher rate and lower concentration than might otherwise be expected.

The second comment is that it was not possible to estimate breathing loss for the tanks, as predictive equations are not available for this situation. The common breathing loss equation cannot cope with a tank of coal tar covered with a layer of water (contaminated with various hydrocarbons). Thus, the emissions estimate for tar storage tanks is probably low.

Emissions from Tar Refining (Topping)

Tar topping at the tested plant was accomplished with a single flash distillation with vacuum provided by steam jets. Chemical oil and an aqueous stream were condensed by indirect cooling in separate exchangers before a barometric condenser final stage. No measurements of this system were made. Evidence that hydrocarbons did get into the water was provided by naphthalene condensation around the vent pipe on the barometric condenser. The rates appeared to be low compared to other emissions in the area.

Tar Distillation Products Storage

The products of the plant's one-stage flash distillation of tar were pitch and chemical oil. No emissions were noted from the pitch handling

TABLE 17. SUMMARY OF ORGANIC ANALYSIS, VAPOR ABOVE TAR STORAGE TANK
Emission rate: 0.14 sm^3/Mg coke

Compounds Identified by GC	Concentration, mg/sm^3	MEGs[a] Category Number	MATE[b] Values, mg/sm^3	Ratio $\left(\frac{\text{Conc. Found}}{\text{MATE}}\right)$
C_1-C_7 HC(Avg. MW≈19)	3.75	1	min. = 32	0.12
Benzene	65.6	15	3	22
Toluene	21.1	15	375	0.06
Xylenes and ethylbenzene	16.3	15	435	0.04
Sulfur compounds (as H_2S)	not detected	53	15	-

Liquid Chromatography	MATE Comparison Value, mg/sm^3	MEGs[a] Category Number	Min. MATE[b] Value in Category	Ratio
Aliphatic hydrocarbons	1.6	1^c	32	0.05^c
Halogenated aliphatics	0.16	2^c	0.1	1.6^c
Aromatic hydrocarbons	*32.1*	*15,21A,22*	*1.0*	*32.1*
Halogenated aromatics	1.45	16^c	0.7	2.1^c
Heterocyclic N, O, S compounds	*1.11*	*23,24,25*	*0.1*	*11.1*
Sulfides, disulfides	1.11	$13B^c$	20	0.06^c
Nitriles	*1.11*	*9*	$1.1[30]^d$	$1.0^c[0.04]^d$
Ethers	19.5	$3,4^c$	0.01	$1,950^c$
Aldehydes, ketones	28.5	7^c	0.2	143^c
Nitroaromatics	0.71	17^c	1.0	0.71^c
Alcohols	8.1	$5,6^c$	10	0.81^c
Amines	1.79	$10^c,11^c,12^c$	0.001	$1,770^c$
Phenols	*6.7*	$18,19^c,20^c$	$0.1[10]^d$	$67^c[0.7]^d$
Esters, amides	30.1	$8C,8D^c$	1.0	30.1^c
Mercaptans	1.1	$13A^c$	1.0	1.1^c
Carboxylic acids	1.1	$8A^c,8B^c$	0.3	3.7^c
Sulfoxides	1.1	14^c	1.0	1.1^c
GRAV conc. in sample	37.0-582 mg/sm^3			
TCO conc. in sample	1,450 mg/sm^3			

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[a] MEG = Multimedia Environmental Goals

[b] MATE = Minimum Acute Toxicity Effluent

[c] Not indicated by GC/MS work

[d] Reflects compounds found by GC/MS work
Italics highlight categories found by GC/MS

TABLE 17. (continued)

IDENTIFICATION

Elution Temperature (°C)	Compound	Elution Temperature (°C)	Compound
70.0	Benzene	122.0	C_2-phenol (?)
70.0	Toluene	122.7	Naphthalene
70.0	Pyridine	124.9	Benzothiophene
77.2	m- and p-Xylenes	131.6	Quinoline
79.5	Styrene[a]	141.2	Methylnaphthalene
80.1	p-Xylene	143.5	Methylnaphthalene
90.7	Benzofuran	153.4	Biphenyl
92.6	Methylpyridines	157.5	C_2-naphthalene
93.9	Benzofuran	159.8	C_2-naphthalene
94.5	C_3-benzenes	163.3	Biphenylene or acenaphthylene (?)
98.7	Phenol	168.1	Acenaphthene
101.5	Indene	173.2	Dibenzofuran
104.4	C_4-benzenes	181.9	Fluorene
107.3	Cresol	190.5	X-methylacenaphthylene
108.9	$C_{10}H_{12}$ isomer	190.5	Aminoethylcarbazole
112.7	Cresol	205.9	Phenanthrene
113.1	Methylindene	207.5	d_{10}-anthracene[b]

QUANTITATION

Of those compounds identified, only quinoline and biphenyl were quantitated. Subjectively, naphthalene appeared to be the prevalent compound.

Compound	Wt. of Compound In XAD Extract (mg)	Wt. of Compound In Canister Rinse (mg)	Total Wt.	Concentration (mg/sm^3) in Gas Sample
Biphenyl	10.4	0.5	10.9	1.9
Quinoline	31.1	1.4	32.5	5.8

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[a] Often an artifact from sample contact with plastics.

[b] Internal standard.

operations; a chemical oil storage tank was sampled. As with the tar storage, the chemical oil tank was a vented, fixed roof tank with additional vents near the top of the tank sidewalls. Naphthalene was condensed on the hatch covers and vents. The tank was maintained above ambient temperature, in the range of 50° C.

The problems associated with estimating breathing loss from this tank include inadequate vapor pressure data and the effect of wind blowing through the side vents. The results of the sampling and analysis are summarized in Table 18. Based on the GC/MS work done on other vapor samples, we might expect that only compounds in MEGs categories 2, 9, 15, 18, 21, and 22 are actually present.

6.3 ENVIRONMENTAL EFFECTS OF AMMONIA PROCESSING

Again, most of the emissions from this processing segment are fugitive. All flushing liquor decanters and tar decanters were included under the "Tar Processing" section above. The company at which the sampling was conducted considered their wastewater treatment plant, including the ammonia recovery portion, to be proprietary, and thus no samples were collected in this portion of the plant. This section will consider ammonia stills (both free and fixed) and ammonium sulfate production. The pollutant sources are:

(1) sulfate drying
(2) sulfuric acid vapor
(3) lime leg muck, and
(4) process fugitives.

Also discussed are emissions from ammonia destruction by incineration. The treatment of waste ammonia liquor in a water treatment plant is discussed in a separate section.

Ammonium Sulfate Drying and Acid Storage

At the tested plant, ammonium sulfate crystals were washed, then centrifuged. The dewatered crystals were then entrained in a heated air conveying system and transported to a storage pile. Emissions (if present, presumably SO_2 and NH_3) from this operation were not determined. The available data are inadequate to predict the emissions from drying ammonium sulfate. The same considerations apply to the acid storage tanks. There was no measurable emission.

TABLE 18. SUMMARY OF ORGANIC ANALYSIS, VAPOR ABOVE CHEMICAL OIL TANK

Emission rate: 0.024sm^3/Mg coke

Compounds Identified by GC	Concentration, mg/sm^3	MEGs[a] Category number	MATE[b] Values, mg/sm^3	Ratio $\left(\frac{\text{Conc. Found}}{\text{MATE}}\right)$
C_1-C_7 HC(Avg. MW≅16)	1.86	1	min. = 32	0.06
Benzene	327	15	3	109
Toluene	266	15	375	0.709
Xylenes and ethylbenzene	200	15	435	0.46
Sulfur compounds (as H_2S)	not detected	53	15	-

Liquid Chromatography	MATE Comparison Value mg/sm^3	MEGs[a] Category Number	Min. MATE[b] Value in Category	Ratio
Aliphatic hydrocarbons	*(34.8)*	*1*	*32*	*1.1*
Halogenated aliphatics	*(3.48)*	*2*	*0.1*	*5*
Aromatic hydrocarbons	*(640)*	*15,21A,22*	*1.0*	*640*
Halogenated aromatics	(57.7)	16	0.7	82
Heterocyclic N, O, S compounds	*(8.64)*	*23,24,25*	*0.1*	*86*
Sulfides, disulfides	(8.64)	13B	20	0.43
Nitriles	*(8.64)*	*9*	*1.1*	*7.8*
Ethers	(186)	3,4	0.01	18,600
Aldehydes, ketones	(165)	7	0.2	825
Nitroaromatics	(4.2)	17	1.0	4.2
Alcohols	(6.3)	5,6	10	0.63
Amines	*(6.3)*	*10,11,12*	*0.001*	*6,300*
Phenols	*(4.9)*	*18,19,20*	*0.1*	*49*
Esters, amides	(165)	8C,8D	1.0	165
Mercaptans	(4.9)	13A	1.0	4.9
Carboxylic acids	*(4.9)*	*8A,8B*	*0.3*	*16.3*
Sulfoxides	(4.9)	14	1.0	4.9
GRAV conc. in sample	860-1,950 mg/sm^3			
TCO conc. in sample	2,050 mg/sm^3			

[a] MEG = Multimedia Environmental Goals

[b] MATE = Minimum Acute Toxicity Effluent

Values in parentheses are partially based on GRAV mass before subtraction of blank.

Italics highlight categories found by GC/MS in other samples.

Lime Leg Muck

The use of lime to reduce the pH of ammoniacal liquor in a fixed still of conventional design coincidentally causes a sludge to form in the dissolver at a rate of around 0.35 kg/Mg coke.[61] The sludge was not sampled during this study. The majority of the sludge is composed of precipitates (calcium salts) formed within the ammonia stills.[62] The extent to which organic pollutants are entrained in the sludge has not been reported. The use of NaOH for pH control does not cause a sludge to form. The method of disposal of this sludge was not determined.

Process Fugitives

There are few opportunities for fugitive emissions from this processing sector. None were identified during the visit other than the acid "odor" mentioned above. There are certainly emissions from ammonium sulfate storage, but these are apparently at a very low level.

6.4 ENVIRONMENTAL EFFECTS OF DEPHENOLIZATION PROCESS

A dephenolization process was not sampled during this study, so all comments made are based on the literature. The primary process wastes are the wastewater after "springing" the tar acids from the sodium salts and the waste/springing gas. If excess ammonia liquor (including 0.14 kg tar acid/Mg coke) contacts light oil which then contacts a 10 percent caustic solution, the water becomes a waste stream once the tar acid is released. At a consumption rate of 1 kg caustic per kg phenol,[62] about 1.26 l of wastewater are produced per Mg coke (0.3 gal/ton). The composition of this wastewater was not available; the expected composition would be primarily sodium salts of the springing gas such as sodium carbonate, bicarbonate, and sulfide.[63] Perhaps 5 percent of the tar acids would remain as phenolic salts. Secondary treatment options have been described in the literature for the recovery of most of these residual phenolics,[60] but their prevalence is not known.

The utilization of an acid gas to release tar acids from the caustic solution is described in the literature.[27 62 63] The rate of emission is not known, nor is the composition. If blast furnace gas at 30 percent CI_3 is used to spring the tar acids, and all CO_2 combines with the sodium, the waste gas rate would be about 0.32 m^3/Mg coke. The rate of organics stripping which would occur is not known. The gases can be vented back to the suction mains.[62]

Emissions from tank vents and separator were not quantified in the literature. As described above, these have been vented back to the suction main. The springing wastes are not included on Figure 15 because "springing" is a seldom used unit process.

6.5 FINAL COOLER AND NAPHTHALENE HANDLING

The plant at which the sampling was done utilized a contact, water type final cooler. Naphthalene separation was by froth flotation with separation in open basins. A package cooling tower was utilized to cool the recirculating water. Other techniques, thought to produce significantly different results, are discussed separately.

The emission sources identified for the contact, recirculating water type final cooler are those associated with the naphthalene separation from the water and emissions from the cooling tower. Naphthalene handling by melting/drying in vented tanks was another significant emission source. The use of tar bottom final coolers and wash oil final coolers was not observed, and only qualitative comments are offered.

Naphthalene Separation

Naphthalene condenses in the final cooler water and is collected as a dirty brown slurry. The plant visited began the separation with a froth flotation operation. Agitators submerged in the liquid drew air into the vortex and dispensed it in the water. The vessel was loosely covered with a series of hatches. No vent stream was at a rate sufficient to be measured, although there were visible wisps of vapor. The vapor directly above this liquid surface was sampled and the results are presented in Table 19. As before, many of the MEGs categories may not be present. The aromatic hydrocarbons are again above the MATE values. The naphthalene slurry which floated to the top of the water was skimmed and collected in open sumps, and the water was passed through a series of small basins to allow additional naphthalene separation.

The rate of emissions from this naphthalene collection operation could not be determined. The total superficial exposed surface area was about

TABLE 19. SUMMARY OF ORGANIC ANALYSIS, FROTH FLOTATION SEPARATOR
Emission rate: unknown

Compounds Identified by GC	Concentration, mg/sm^3	MEGs[a] Category Number	MATE[b] Values, mg/sm^3	Ratio $\left(\frac{\text{Conc. Found}}{\text{MATE}}\right)$
C_1-C_7 HC(Avg. MW≅24)	2,051	1	min. = 32	64
Benzene	4,700	15	3	1,570
Toluene	488	15	375	1.3
Xylenes and ethylbenzene	82.1	15	435	0.2
Sulfur compounds (as H_2S)	2,125	53	15	140

Liquid Chromatography	MATE Comparison Value, mg/sm^3	MEGs[a] Category Number	Min. MATE[b] Value in Category	Ratio
Aliphatic hydrocarbons	*(11.7)*	*1*	*32*	*0.36*
Halogenated aliphatics	*(1.18)*	*2*	*0.1*	*11.8*
Aromatic hydrocarbons	*(33.8)*	*15,21A,22*	*1.0*	*33.8*
Halogenated aromatics	(1.69)	16	0.7	2.41
Heterocyclic N, O, S compounds	*(1.07)*	*23,24,25*	*0.1*	*10.7*
Sulfides, disulfides	(1.07)	13B	20	0.05
Nitriles	*(1.07)*	*9*	*1.1*	*1.0*
Ethers	(22.2)	3,4	0.01	2,220
Aldehydes, ketones	(39.9)	7	0.2	200
Nitroaromatics	(0.96)	17	1.0	1.0
Alcohols	(12.8)	5,6	10	1.28
Amines	*(3.4)*	*10,11,12*	*0.001*	*3,400*
Phenols	*(5.8)*	*18,19,20*	*0.1*	*58*
Esters, amides	(43.5)	8C,8D	1.0	43.5
Mercaptans	(1.2)	13A	1.0	1.2
Carboxylic acids	*(1.2)*	*8A,8B*	*0.3*	*4*
Sulfoxides	(1.2)	14	1.0	1.2
GRAV conc. in sample	18.9-19.9 mg/sm^3			
TCO conc. in sample	660 mg/sm^3			

[a] MEG = Multimedia Environmental Goals

[b] MATE = Minimum Acute Toxicity Effluent

Values in parentheses are based on GRAV mass before subtraction of blank.

Italics highlight categories found by GC/MS in other samples.

1,000 ft^2. The actual surface exposed to the wind by the crystalline slurry is not known. The rate of entrained air flow in the froth flotation vessel was not available from the plant. Subjectively, the odor of naphthalene was quite strong in this area of the plant.

Final Cooler Cooling Tower Emissions

The final cooler cooling tower has for some time been recognized as a potential source of cyanide emissions, and was sampled both for cyanide and organics. The level of cyanide in the water depends on the degree of cyanide stripping which is accomplished in the ammonia stills, along with final cooler operations and coal composition. At the site sampled, hydrogen cyanide was present in the gas leaving the cooling tower at an average concentration of 76.5 ppm, which corresponds to a mass emission of 0.28 kg/Mg coke (0.56 lb/ton). Based on the literature values of hydrogen cyanide production given in Chapter 4, 0.71 kg/Mg coke (0.5 kg/Mg coal), this source accounts for about half the cyanogen generated. The gas flow rate was estimated by assuming that the gas mass flow was equal to the known liquid circulation rate. Organic emissions were also measured and are presented in Table 20. Again, several categories were not indicated by the GC/MS work. Based on the MATE values, emissions of significance from this source are benzene and hydrogen cyanide. In addition to the vapor phase measurements, liquid samples were collected from both the hot and cold wells of the cooling tower. These were subjected to the Level 1 organic analysis protocol, and the results are summarized in Table 21.

Naphthalene Processing

Naphthalene collected as described above is impure and in roughly a 60 percent water slurry. This naphthalene slurry was pumped into a horizontal cylindrical tank. Once the tank was full, the water was decanted. Steam coils within the vessel were then utilized to dry and melt the naphthalene. This operation continued for one to two days. There was not a suitable sampling point for the vapor emission from this process; scaffolding would have been required. The vent rate was estimated to be 2.9 sm^3 vapor/Mg coke (93.4 scf/ton) by measuring the rate of air entering the vessel due to the chimney effect. The temperature in the tank was 101° C. Naphthalene was sampled at a concentration of 533 g/sm^3, which amounts to 1.56 kg naphthalene per Mg coke

TABLE 20. SUMMARY OF ORGANIC ANALYSIS, FINAL COOLER COOLING TOWER VAPOR
Emission rate: 3,230 sm^3/Mg coke

Compounds Identified by GC	Concentration, mg/sm^3	MEG's Category Number	MATE[b] Values, mg/sm^3	Ratio $\left(\frac{\text{Conc. Found}}{\text{MATE}}\right)$
C_1-C_7 HC (Avg. MW≅16)	1.89	1	min. = 32	0.06
Benzene	15.8	15	3	5.3
Toluene	not detected	15	375	-
Xylenes and ethylbenzene	not detected	15	435	-
Sulfur compounds (as H_2S)	3.3	53	15	0.2

Liquid Chromatography	MATE Comparison Value, mg/sm^3	MEG's[a] Category Number	Min. MATE[b] Value in Category	Ratio
Aliphatic hydrocarbons	*(1.90)*	*1*	*32*	*0.06*
Halogenated aliphatics	*(0.08)*	*2*	*0.1*	*0.8*
Aromatic hydrocarbons	*(4.76)*	*15,21A,22*	*1.0*	*4.76*
Halogenated aromatics	(0.21)	16[c]	0.7	0.3[c]
Heterocyclic N, O, S Compounds	*(0.08)*	*23,24,25*	*0.1*	*0.8*
Sulfides, disulfides	(0.09)	13B[c]	20	0.004[c]
Nitriles	*(0.08)*	*9*	*1.1*	*0.07*
Ethers	(2.38)	3[c],4[c]	0.01	238
Aldehydes, ketones	(3.68)	7[c]	0.2	18.4[c]
Nitroaromatics	*(0.17)*	*17*	*1.0*	*0.17*
Alcohols	(1.42)	5[c],6[c]	10	0.14[c]
Amines	*(0.25)*	*10,11[c],12[c]*	*0.001[19][d]*	*250[0.01][d]*
Phenols	*(0.21)*	*18,19[c],20[c]*	*0.1[10][d]*	*2.1[c][0.02][d]*
Esters, amides	(3.68)	8C[c],8D[c]	1.0	3.68[c]
Mercaptans	(0.21)	13A[c]	1.0	0.21[c]
Carboxylic acids	*(0.21)*	*8A,8B*	*0.3*	*0.7*
Sulfoxides	(0.21)	14[c]	1.0	0.21[c]
GRAV conc. in sample	2.75-10.6 mg/sm^3			
TCO conc. in sample	226 mg/sm^3			

[a] MEG = Multimedia Environmental Goals

[b] MATE = Minimum Acute Toxicity Effluent

Values in parentheses are based on GRAV mass before substraction of blank.

[c] Not indicated by GC/MS work

[d] Reflects compounds found by GC/MS work

Italics highlight categories found by GC/MS.

TABLE 20. (continued)

IDENTIFICATION

Elution Temperature (°C)	Compound	Elution Temperature (°C)	Compound
100.0	1,1,1-Trichloroethane	125.1	Methyl indenes
100.0	Benzene	128.3	C_2-phenols
100.0	Cyclohexene	129.3	Naphthalene
100.0	Pyridine	137.0	Quinoline
100.0	Toluene	144.0	Methylbenzothiophene isomer
100.0	X-methylpyridines	145.3	Methylnaphthalene
100.0	Xylenes	147.5	Methylnaphthalene
100.0	Phenylacetylene (?)	151.7	Indole
100.0	C_2-pyridines	156.8	Biphenyl
100.0	Styrene[a]	161.3,163.2	C_2-naphthalene isomers
102.1	C_2-pyridine		
105.6	Benzonitrile	166.7	Biphenylene
106.9	Aniline	171.5,171.9	$C_{13}H_{12}$ and $C_{14}H_{14}$ isomers,
		172.9	acenaphthene
107.9	Benzofuran	176.3	Dibenzofuran
108.8	C_2-pyridine (?)	186.3	Fluorene
109.8	Phenol	193.9,198.1	Amino ethylcarbazole (?)
112.7	Indene	210.3	Phenanthrene
115.5	C_7H_9N isomer	210.6	D_{10}-anthracene
116.2	Cresols	265.0	a phthalate[a]
118.1	$C_{10}H_{12}$ isomer	265.0	a phthalate[a]

QUANTITATION

Of those compounds identified, only quinoline and biphenyl were quantitated. Subjectively, naphthalene appeared to be the prevalent compound.

Compound	Wt. of Compound In XAD Extract (mg)	Wt. of Compound in Canister Rinse (mg)	Total Wt.	Concentration (mg/sm^3) in Gas Sample
Biphenyl	1.7	0	1.7	0.06
Quinoline	10.2	0	10.2	0.37

[a] Often an artifact from sample contact with plastics.

[b] Internal standard.

TABLE 21. ORGANIC EXTRACT SUMMARY, FINAL COOLER COOLING TOWER - HOT AND COLD WELLS

	Preliminary	Concentrate	LC1	LC2	LC3	LC4	LC5	LC6	LC7
Hot Well									
pH 2 extract									
Total organics, mg/l	311	241	3.3	81	0.53	12.6	2.9	84.4	1.4
TCO, mg/l	2,160	1,463	0.0	79	0.0	11	2.9	76	0.0
GRAV, mg/l	192	362	3.3	2.1	0.53	1.6	0.0	8.4	1.6
pH 12 extract									
Total organics, mg/l	106	121	0.0	3.8	0.26	4.6	1.3	74.4	0.0
TCO, mg/l	720	660	0.0	3.8	0.0	3.8	1.3	55.1	0.0
GRAV, mg/l	80	258	0.0	0.0	0.26	0.80	0.0	19.3	0.0
Hot Well Total Organics, mg/l	417	362	3.3	84.8	0.79	17.2	4.2	159	1.6
Cold Well									
pH 2 extract									
Total organics, mg/l	201	161	2.0	27.0	1.0	4.2	10.6	90.4	0.53
TCO, mg/l	1,360	863	0.0	27.0	0.0	3.2	9.0	74	0.0
GRAV, mg/l	160	358	2.0	0.0	1.0	1.0	1.6	16.4	0.53
pH 12 extract									
Total organics, mg/l	84.5	51	0.0	0.07	0.13	1.4	0.72	34.9	0.0
TCO, mg/l	480	356	0.0	0.07	0.0	1.0	0.59	31.6	0.0
GRAV, mg/l	160	29	0.0	0.0	0.13	0.40	0.13	3.3	0.0
Cold Well Total Organics, mg/l	286	212	2.0	27.1	1.13	5.6	11.3	125	0.53

(3.13 lbs/ton), or about twice the plant's total naphthalene production. The sample is obviously not representative of the average emission rate, and emissions from this source cannot be quantitated on the basis of the available data.

Once-Through Cooling Water

A plant which utilized once-through cooling water in the final cooler would produce an aqueous waste very similar to that described as the cooling tower hot well, above.

Tar Bottom Final Cooler

No sampling was conducted at a tar bottom final cooler. The emissions from naphthalene handling would be absent in this case, and cooling tower emissions should be similar to those discussed above. A blowdown will still be required for the recirculating water.

Wash Oil Final Cooler

Emissions from a wash oil final cooler were not determined. Qualitatively, wash oil coolers provided the wash oil is itself in noncontact heat exchangers and that naphthalene is processed in closed vessels, should have very low emission rates. A wastewater stream will be condensed as the cooler oven gas is cooled, and this will require treatment. In addition, the distribution of HCN in the plant will probably be different (higher HCN in the gas) than it would be in a water type final cooler, and this may cause problems downstream.

6.6 ENVIRONMENTAL EFFECTS OF LIGHT OIL RECOVERY

The emissions identified with light oil recovery include a sludge, several decanted water streams, fugitive tank emissions, and a vent from the light oil condenser.

Wastewater Streams

Several wastewater streams are decanted in the light oil plant. The primary source of the water is the line steam used to strip light oil from wash oil, and water must be separated from all the hydrocarbon liquids condensed from the still vapor as well as from wash oil. None of these water streams were analyzed. They are commonly collected in the "intercepting sump" and treated in the combined wastewater treatment plant. The rate has been estimated at between 100 and 500 l/Mg coke depending on the ability of the operator to tightly recycle the water.

Wash Oil Sludge

A sludge forms in wash oil as it is used over and over again. The sludge was not analyzed and the rate of formation was not determined. The muck consists of polymers formed by the interaction of organic mercaptans, disulfides, heterocyclic sulfur compounds, and unsaturated hydrocarbons, along with oils, dirt, and water.[16] Other reactions also form sludges. Disposal can be to landfill or on to the coal pile for recycle to the ovens.

Fugitive Tank Emissions

Fugitive emissions occur from wash oil storage, wash oil decanters, and light oil storage. Only the light oil storage tank was sampled, as it was amenable to data reduction by the tank breathing loss equation. No emissions with measurable rates were present. Results of the samples from the light oil storage tank are presented in Table 22.

Light Oil Condenser Vent

The noncondensibles vent off the light oil condenser was not accessible under Level 1 constraints and was not sampled. No data are available in the literature. This stream probably consists of the fraction of the coke oven gas which dissolved in the wash oil, as well as light oil vapor. This stream is thought to be quite small, appropriate for the 2-inch pipe used to vent the condenser.

6.7 DESULFURIZATION - ENVIRONMENTAL ASSESSMENT

A great deal of research, development, engineering, and regulatory effort is presently being expended on the desulfurization of coke oven gas. In the interest of making the best use of available resources and to avoid duplication, no samples of desulfurization plant streams were taken. This section is a review of the extensive literature on desulfurization.

The intent of desulfurization of coke oven gas is to reduce the emissions of SO_x into the ambient air when the coke oven gas is burned. As has been

TABLE 22. SUMMARY OF ORGANIC ANALYSIS, LIGHT OIL STORAGE

Emission Rate: 15.6 sm^3/Mg coke

Compounds Identified by GC	Concentration mg/sm^3	MEG's Category[a] Number	MATE Value[b] (mg/sm^3)	Ratio $\left(\frac{\text{Found}}{\text{MATE}}\right)$
C_1-C_7 HC (Average MW≅46)	225	1	min. = 32	7
Benzene	1,040	15	3	347
Toluene	36.8	15	375	0.1
Xylenes and ethylbenzene	not detected	15	435	---
Sulfur compounds (as H_2S)	37-44	53	15	2.5-2.9

[a] MEG = Multimedia Environmental Goals.

[b] MATE = Minimum Acute Toxicity Effluent.

stated, the common techniques convert the sulfur to either the elemental form or to sulfuric acid. With respect to overall removal then, both the efficiency of removal of sulfur from coke oven gas and the efficiency of converting this sulfur to the desired product must be considered. In addition, the desulfurization processes themselves are not without environmental impact.

Vacuum Carbonate System

The Koppers' Vacuum carbonate system, as offered in the mid-1950's, had a H_2S removal efficiency of about 90 percent. Changes in the processing rates allowed an increase in efficiency to about 93 percent at the cost of increased utilities consumption. A further process modification has given the new two-stage vacuum carbonate process an H_2S removal of around 98 percent without a further increase in utilities consumption.

Recognition that organic sulfur not removed by the vacuum carbonate system accounts for about 5 percent of the sulfur in coke oven gas requires that the overall efficiencies be reduced to 86 to 93 percent.

Spent absorbing solution from vacuum carbonate plants must be periodically replaced. The rate is variable; one plant has run three years before replacing the solution, while another has had to replace the solution every 8 months. Thiocyanate and thiosulfate salts, as well as iron-sulfur-cyanide compounds are the major contaminants. Further quantification of this stream was not available in the literature. Reduced contamination of the carbonate solution is claimed if oxygen and ammonia in the gas and absorbent solution are minimized.

Ejector jet condensate is the second major vacuum carbonate system discharge. The volume of this waste (roughly 40 l/Mg coal charged[64]) could be greatly reduced or eliminated by the use of mechanical ejectors rather than steam jets, as was once standard.[14]

Sulfiban System

The Sulfiban system can be operated up to about 98 percent efficiency, and is the only common desulfurization technique that removes both organic and inorganic sulfur from coke oven gas. The major liquid waste from the Sulfiban system is spent absorbing solution; the rate of purge is around 140 l/day in a 5,000 Mg coal/day coke plant. The purge is a sludge containing FeS, Prussian

Blue, thiourea,[64] and a gummy material apparently formed by reaction between HCN and the amine. It has been reported that this sludge can be disposed of in the sinter plant.[64]

Dravo/Still Process

The Dravo/Still H_2S removal system is offered in two versions which reduce the H_2S content of the coke oven gas to 35-50 gr H_2S/100 scf (90-93 percent efficiency for 500 gr H_2S loading) and 10 gr H_2S/100 scf (98 percent removal), respectively. Organic sulfur is not removed. H_2S removal then ranges from 90 to 98 percent, and overall desulfurization from around 86 to 93 percent. No secondary environmental effects have been reported for the Dravo/Still process.

Stretford Process

The Stretford process is another H_2S absorber with a very high (99+ percent) H_2S removal efficiency. The process produces elemental sulfur directly, so no auxiliary acid gas treatment (Claus Plant or acid plant) is required. The Stretford process has a significant secondary effluent problem with the by-product thiocyanates and thiosulfates formed by the reaction of HCN with the absorbing solution. Some treatment processes produce a purge stream eventually while another incinerates portions of the waste. Present emphasis is on the incinerator approach. No data or emissions from the incinerator were available in the literature.

Claus Sulfur Plants

Claus sulfur plants convert the incoming acid gas to elemental sulfur with efficiencies of roughly 95 to 98 percent. Tail gas from a Claus plant can be treated in one of several available tail gas treatment systems, giving overall efficiencies of 99 percent. Documented Claus plant performance at by-product plants has been more like 95 percent efficiency. Following tail gas treatment, the gas stream is usually incinerated, converting any residual sulfur to SO_2.

Sulfuric Acid Plants

The overall efficiency of single-stage sulfuric acid plants is around 97 percent. Double stage plants or plants with tail gas treatment can exceed 99 percent efficiency.

6.8 ENVIRONMENTAL EFFECTS OF WASTEWATER PROCESS

As has been discussed, wastewater treatment in the by-product coke industry varies considerably. The principal effluent, of course, depends on the process. The primary source of water to the treatment plant is excess ammonia liquor, a Level 1 analysis of which is presented in Table 23. The pollutants from a biological treatment plant are vapor off the holding tanks and aeration basins, the biological sludge, and whatever is left in the effluent water.

Biological Sludge

The sludge from the sampled plant was analyzed for both elemental and organic components as directed by the Level 1 protocol. The elemental analysis is presented in Table 24. Organic analysis results are presented in Table 25. The sludge was produced at a rate of 1.7 kg/Mg coke, and was removed from the plant by a contractor. Some potential problem areas are identified by the Level 1 analysis.

Vapor off the Holding Tanks and Aeration Basins

Vapor emissions from these sources were not measured. The only source of information located[65] documented batch stripping of coke plant wastewater with air for 10 days. The results were a 15 percent reduction in organic carbon and a 30 percent reduction in cyanide. The authors felt that this was higher than would be encountered in a biological plant, and concluded that stripping would not be significant. Ammonia was not stripped to a measurable degree in this test.

Effluent from Biological Plant

The feed and effluent of a biological treatment plant was analyzed by the Cyrus Rice Corporation for the U.S. EPA under a separate contract.[66] All contaminated coke plant wastewater was fed to the biological plant. The samples were 24 hour integrated samples taken on 3 consecutive days. Preliminary results of this analysis are presented in Table 26. The data are still being analyzed and some values may change.

TABLE 23. ORGANIC EXTRACT SUMMARY, AMMONIA LIQUOR

	TCO (mg)	GRAV (mg)	Total Organics (mg/l)
Preliminary	10,700	7,720	2,420
Concentrate	5,950	6,420	1,630
LC1	730	1,890	346
LC2	4,300	900	687
LC3	315	740	139
LC4	260	320	77
LC5	70	0	9.2
LC6	3,180	1,190	577
LC7	0	130	17
Σ	8,855	5,170	1,850

Comments

pH 2 extract: The pH 2 extract contained about 80 percent of the ammonia liquor organics. Specific coal tar PNA's identified by LRMS at relative intensities of 100 and 10; these included pyrene, perylene, benzpyrene, chrysene, anthracene and others. Other compounds found were polycyclic amines and substituted phenol.

pH 12 extract: Most of this sample was found in LC cut 6, which was complex and difficult to analyze. Aromatic and aliphatic character was detected along with hydroxyl and ketone/ester bands.

TABLE 24. SSMS* ANALYSIS OF BIOLOGICAL PLANT SLUDGE SAMPLE

Element	Value (ppm)	Element	Value (ppm)	Element	Value (ppm)
U	< 0.025	Ce	0.011	Ga	< 0.021
Th	< 0.023	La	< 0.014	Zn	2.0
Bi	< 0.021	Ba	0.27	Cu	1.3
Pb	0.18	Cs	0.004	Ni	14.
Tl	< 0.020	I	< 0.03	Co	0.16
Au	< 0.020	Te	< 0.013	Fe	210.
Ir	< 0.019	Sb	0.014	Mn	5.2
Os	< 0.019	Sn	0.10	Cr	0.071
Re	< 0.019	In	IS†	V	0.025
W	< 0.018	Cd	0.19	Ti	0.30
Hf	< 0.018	Pd	< 0.011	Ca	0.21 %
Lu	< 0.017	Rh	< 0.010	K	12.
Yb	< 0.017	Ru	< 0.010	Cl	270.
Tm	< 0.017	Mo	0.065	S	0.13 %
Er	< 0.017	Nb	0.003	P	27.
Ho	< 0.016	Zr	0.030	Si	32.
Dy	< 0.016	Y	0.006	Al	24.
Tb	< 0.016	Sr	0.95	Mg	96.
Gd	< 0.016	Rb	0.090	Na	0.10 %
Eu	< 0.015	Br	3.0	F	26.
Sm	< 0.015	Se	6.4	B	0.69
Nd	< 0.014	As	2.5	Be	0.006
Pr	< 0.014	Ge	0.81	Li	0.23

*SSSMS - Spark Source Mass Spectrometer
†IS - Internal Standard

TABLE 25. SUMMARY OF ORGANIC ANALYSES, BIOLOGICAL TREATMENT PLANT SLUDGE

Liquid Chromatography	MATE Comparison Value,[c] mg/kg	MEG's Category Number	Min. MATE Value in Category	Ratio
Aliphatic hydrocarbons	2.1	1	None published	None published
Halogenated aliphatics	0.2	2	20	0.01
Aromatic hydrocarbons	6.45	15,21A,22	0.003	2,150
Halogenated aromatics	0.13	16	0.00001	13,000
Heterocyclic N, O, S compounds	0.025	23,24,25	3.0	0.008
Sulfide, disulfides	0.025	13B	None published	-
Nitriles	0.025	9	2.0	0.012
Ethers	3.32	3,4	20	0.17
Aldehydes, ketones	3.5	7	0.2	17.5
Nitroaromatics	0.3	17	2.0	0.15
Alcohols	3.00	5,6	2.0	1.5
Amines	0.30	10,11,12	0.04	7.5
Phenols	3.2	18,19,20	0.01	320
Esters, amides	3.5	8C,8D	0.003	1,170
Mercaptans	0.33	13A	30	0.01
Carboxylic acids	2.73	8A,8B	2.0	1.4
Sulfoxides	0.03	14	1,200	0.00002
GRAV conc.	5.9 - 7.4 mg/kg			
TCO conc.	0.4 - 17.8 mg/kg			

[a] MEG = Multimedia Environmental Goals.

[b] MATE = Minimum Acute Toxicity Effluent.

[c] Sludge density assumed to be 1 g/ml.

TABLE 26. BIOLOGICAL TREATMENT PLANT TESTING–SELECTED RESULTS[1]

COMPONENT	UNITS	AVERAGE OF 3 SAMPLES FEED	AVERAGE OF 3 SAMPLES EFFLUENT
Ammonia	mg/l	26	0.73
Organic carbon	mg/l	383	53
Chloride (diss.)	mg/l	371	202
Cyanide Amenable to Chlorination	mg/l	0.48	0.33
Total cyanide	mg/l	2.74	2.34
Cyanide (AISI)	mg/l	0.18	0.07
Nitrogen (Kjeldahl)	mg/l	102	10.9
Suspended solids	mg/l	79	39
Solvent extract (oil) EPA method	mg/l	20	4.3
Sulfate (diss.)	mg/l	202	342
Sulfide	mg/l	153	<0.3
Thiocyanate (SCN)	mg/l	197	0.73
Cyanate (CNO)	mg/l	3.6	0.35
Phenolic compounds (phenol)	mg/l	231	0.028
pH		11.2	7.4
Organic compounds[2]		Range from 3 Samples	
acenaphthene	ppb	0	1-6
benzene	ppb	0 < 350	<1 to <371
carbon tetrachloride	ppb	0	0 to 9
chlorobenzene	ppb	0 to 250	159 to 264
hexachlorobenzene	ppb	0 to 17,100	46 to 82
1,1,2,2-tetrachloroethane	ppb	0 < 900	<3 to <820
2-chloronaphthalene	ppb	0 to 160	0
2,4,6-trichlorophenol	ppb	ND	ND
parachlorometa cresol	ppb	ND to 2,130	10 to 168
chloroform	ppb	0 to < 3,800	9 to <990
2-chlorophenol	ppb	ND	ND
1,1-dichloroethylene	ppb	0 to <4,600	0 to <1,205
2,4-dichlorophenol	ppb	ND to 4,500	ND
2,4-dinitrotoluene	ppb	0	<7 to 10
2,6-dinitrotoluene	ppb	0 to 29,700	0 to <7
1,2-diphenylhydrazine	ppb	0	0 to 137
ethylbenzene	ppb	0 to 100	
fluoranthene	ppb	0 to 190	0 to 12
2-nitrophenol	ppb	ND	ND
4-nitrophenol	ppb	ND	ND
2,4-dinitrophenol	ppb	ND	ND
4,6-dinitro-o-cresol	ppb	ND	ND
pentachlorophenol	ppb	ND	ND to 93
phenol	ppb	112,000 to 131,500	ND to 35
bis(2-ethylhexyl)phthalate	ppb	0 to 29,000	0 to 39
butyl benzyl phthalate	ppb	200 to 8,600	2 to 85
di-n-butyl phthalate	ppb	40 to 12,100	14 to 22
di-n-octyl phthalate	ppb	0 to 350	0 to 320
dimethyl phthalate	ppb	0	0 to 53
benzo(a)anthracene	ppb	0 to 2,270	0 to 24
benzo(a)pyrene	ppb	0 to 330	0 to 44
3,4-benzofluoranthene	ppb	0 to <140	0 to <6
benzo(k)fluoranthene	ppb	0 to <140	0 to <6
chrysene	ppb	0 to 3,800	0 to 14
acenaphthylene	ppb	90 to 34,900	0 to 6
anthracene	ppb	<200 to <1,000	0 to <239
benzo(gni)perylene	ppb	0	0 to <1
fluorene	ppb	0 to <1,000	5 to 9
phenanthrene	ppb	<200 to <1,000	0 to <239
dibenzo(a,h)anthracene	ppb	0	0 to <1
indene(1,2,3-cd)pyrene	ppb	0	0 to <1
pyrene	ppb	0 to 280	16 to 38
tetrachloroethylene	ppb	0 to <650	0 to <580
toluene	ppb	0 to 120	0 to 100
trichloroethylene	ppb	0 to <100	0 to <1,148

NOTES: [1] These are preliminary data released by the Effluent Guidelines Division, U.S. EPA.[64]

[2] ND indicates not detected in one of the three samples. "0" indicates that no evidence was found, but that noise in the spectrum prevents a clear ND.

6.9 AMBIENT AIR ANALYSIS - BY-PRODUCT PLANT

Upwind-downwind ambient sampling was conducted at the plant in two separate programs. Hydrogen cyanide was collected in 24-hour integrated samples and 4-hour Level 1 organic runs were made on one day.

Cyanide Analysis

The results of the cyanide analysis are summarized in Table 27, which also shows the orientation of the samples and the daily wind roses. On the two days in which the wind blew across the plant from a roughly constant direction, the cyanide in the air increased roughly one order of magnitude, from an average of 0.006 vppm upwind to an average of 0.062 vppm downwind.

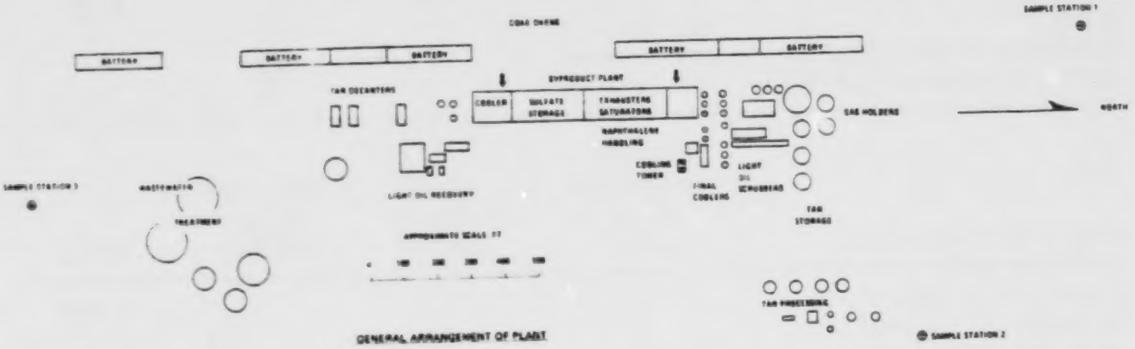
Ambient Organic Vapor Analysis

Ambient organic vapor samples were taken for 4 hours, the downwind sample first and the upwind second. The results are summarized in Tables 28 and 29. The GC results show a slight increase in the ambient benzene concentration, from 0.6 to 0.8 vppm across the plant but the downwind samples were 0.3 and 1.3 vppm--inconsistent. The downwind sample had inadequate organic mass for the liquid chromatography. As can be seen, more organics were collected on the XAD resin upwind of the plant than downwind. The upwind sample point was close to a railroad, which may have had some impact.

6.10 RELATIVE HAZARD OF BY-PRODUCT PLANT SOURCES

The large amount of data relating to emissions to the three media are difficult to evaluate. In this section the relative hazard of the sources (i.e., relative to each other) is developed. The procedure used is essentially a continuation of the techniques used earlier. The ratios of the MATE values for a source were first totalled by category. These ratios were defined as hazard units. The hazard units were then summed across the categories to arrive at a total of hazard units for the source emission (based on a volume or mass). Each source for which these provided sufficient data was treated in this way. For the "Heavy Organics" category, only compounds confirmed by GCMS were included. The data base was incomplete in one or more categories for all of the sources.

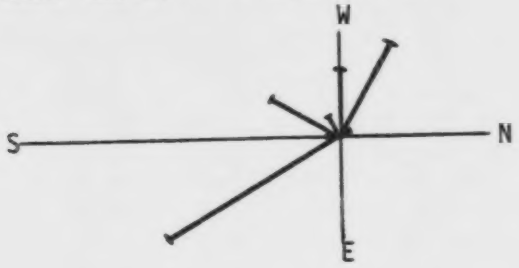
TABLE 27. AMBIENT CYANIDE ANALYSIS


COAL CHARGE
BATTERY
BATTERY
BATTERY
BATTERY
BATTERY
SAMPLE STATION 1
BYPRODUCT PLANT
TAR DECANTERS
COOLER
SULFATE STORAGE
SATURATORS
NAPHTHALENE HANDLING
GAS HOLDERS
NORTH
COOLING TOWER
FINAL COOLING
LIGHT OIL SCRUBBERS
TAR STORAGE
SAMPLE STATION 3
WASTEWATER TREATMENT
LIGHT OIL RECOVERY
APPROXIMATE SCALE FT
0
100
200
300
400
500
TAR PROCESSING
SAMPLE STATION 2

GENERAL ARRANGEMENT OF PLANT

Relative duration of wind from indicated direction.

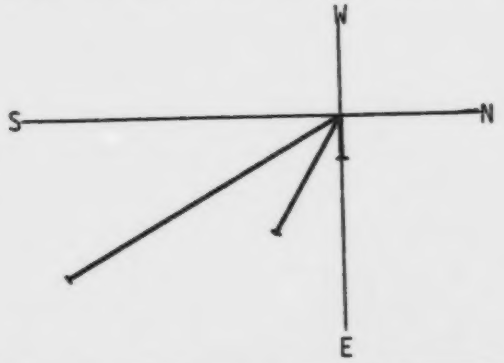
1500 12/13/77 to 1500 12/14/77



Station 1 Downwind -0.069 vppm

Station 3 Upwind -0.008 vppm

1500 12/12/77 to 1500 12/13/77



Station 1 (Downwind) -0.056 vppm

Station 3 (Upwind) -0.004 vppm

TABLE 28. SUMMARY OF ORGANIC ANALYSIS, UPWIND AMBIENT

Compounds Identified by GC	Concentration, mg/sm^3	MEGs[a] Category Number	MATE[b] Value, mg/sm^3	Ratio (Conc. Found / MATE)
C_1-C_7 HC (Avg. MW = 16)	1.9	1	min. = 32	0.06
Benzene	1.95	15	3	0.65
Toluene	not detected	15	375	--
Xylenes and ethylbenzene	not detected	15	435	--
Sulfur compounds (as H_2S)	not detected	53	15	--

Liquid Chromotography	MATE Comparison Value mg/sm^3	MEGs[a] Category Number	Min. MATE[b] Value in Category	Ratio
Aliphatic hydrocarbons	*0.12*	*1*	*32*	*0.004*
Halogenated aliphatics	--	2	0.1	--
Aromatic hydrocarbons	*0.32*	*15, 21A, 22*	*1.0*	*0.32*
Halogenated aromatics	0.02	16	0.7	0.03
Heterocyclic N, O, S compounds	--	*23, 24, 25*	*0.1*	--
Sulfides, disulfides	--	13B	20	--
Nitriles	--	*9*	*1.1*	--
Ethers	0.33	3, 4	0.01	33
Aldehydes, ketones	0.20	7	0.2	1.0
Nitroaromatics	*0.01*	*17*	*1.0*	*0.01*
Alcohols	0.03	5, 6	10	0.003
Amines	*0.03*	*10, 11, 12*	*0.001*	*30*
Phenols	*0.03*	*18, 19, 20*	*0.1*	*0.3*
Esters, amides	0.33	8C, 8D	1.0	0.33
Mercaptans	0.03	13A	1.0	0.03
Carboxylic acids	*0.03*	*8A, 8B*	*0.3*	*0.1*
Sulfoxides	0.03	14	1.0	0.03

GRAV conc. in sampled gas 0.8--1.4 mg/sm^3
TCO conc. in sampled gas 3.6 mg/sm^3

[a] MEG = Multimedia Environmental Goals.

[b] MATE = Minimum Acute Toxitity Effluent.

Italics highlight categories found by GC/MS in some samples.

TABLE 29. SUMMARY OF ORGANIC ANALYSIS, DOWNWIND AMBIENT

Emission Rate Compounds Identified by GC	Concentration, mg/sm^3	MEGs[a] Category Number	MATE[b] Value, mg/sm^3	Ratio $\left(\frac{\text{Conc. Found}}{\text{MATE}}\right)$
C_1-C_7 HC (Avg. MW $\cong$ 16)	2.2	1	min. = 32	0.07
Benzene	2.4	15	3	0.8
Toluene	not detected	15	375	--
Xylenes and ethylbenzene	not detected	15	435	--
Sulfur compounds (as H_2S)	not detected	53	15	--

Liquid Chromatography	MATE Comparison Value mg/sm^3	MEGs[a] Category Number	Min. MATE[b] Value in Category	Ratio
Aliphatic hydrocarbons				
Halogenated aliphatics				
Aromatic hydrocarbons				
Halogenated aromatics				
Heterocyclic N, O, S compounds				
Sulfides, disulfides		INSUFFICIENT ORGANIC MASS NO LIQUID CHROMATOGRAPHY		
Nitriles				
Ethers				
Aldehydes, ketones				
Nitroaromatics				
Alcohols				
Amines				
Phenols				
Esters, amides				
Mercaptans				
Carboxylic acids				
Sulfoxides				
GRAV conc. in sampled gas	1.2--2.2 mg/sm^3			
TCO conc. in sampled gas	0--0.1 mg/sm^3			

[a] MEG = Multimedia Environmental Goals.

[b] MATE = Minimum Acute Toxicity Effluent.

The emission rate for the source was then taken into account by multiplying the total of hazard units per scm, ℓ, or kg by the emission rate in scm/Mg, ℓ/Mg, or kg/Mg to arrive at the weighted total hazard units per Mg of coal fed to the ovens.

The results of this procedure are presented in Table 30. As with the other data manipulations which are based on the MATE values, this procedure is very sensitive to the presence of certain compounds (primarily PNA's) which have very low MATE values (i.e., are considered to be very hazardous). For instance, benzo(a)pyrene, at a median concentration of 22 parts per billion, accounts for nearly 75 percent of the total hazard units attributed to the biological treatment plant effluent. Similar impact for the PNA's is present for several other sources.

TABLE 30. ESTIMATED RELATIVE HAZARD OF COKE BY-PRODUCT PLANT SOURCES

Operation Emission Source	Source Emission Rate Per Mg Coal Fed	Ratios of Concentrations[a] to MATE Values (Defined as Hazard Units, HU)							Total Hazard Units Per scm, ℓ, or kg	Total Hazard Units Per Mg Coal	Normalized Relative Hazard[b]
		Light Aromatics (BTX)	Heavy Organics including PNA's	NH_3	Gaseous S Compounds	Cyanides	Phenols	Biphenyl & Quinoline			
Tar processing											
decanter vapor	1.5 scm	2,430	519	ND	394	ND	0.6	22.1	3,366	5,050	0.036
dewatering/ storage vapor	0.1 scm	22.1	43	ND	NTD	NTD	0.7	2.3	68	6.8	≈0
primary cooler condensate tank vapor	1.2 scm	1,745	ND	ND	222	NTD	ND	ND	1,967	2,400	0.017
distillation product storage vapor	0.02 scm	110	7,056	ND	ND	NTD	49	ND	7,215	140	0.001
Ammonia processing											
excess ammonia liquor	102 ℓ	Not an emission - treated in biotreatment plant									
Final cooler and napthalene handling											
cooling tower for contact cooler, gas	2,307 scm	5.3	7.4	ND	0.02	8.4	0.02	0.08	21.2	49,000	0.349
napthalene separator vapor	rate too low to measure	1,567	3,462	ND	142	ND	58	ND	5,229	-	-
napthalene dryer vapor	2.1 scm	Sample results unreasonable and not representative									
Light oil recovery											
wastewater (wash oil, sludge)	70-360 ℓ	Not an emission - treated in biotreatment plant									
light oil storage vapor	11.1 scm	346	ND	ND	2.6	ND	ND	ND	349	3,900	0.028
Wastewater											
biotreatment plant effluent	335-900 ℓ	0.2	77	NA	ND	NA	21.4	ND	98.6	61,000	0.434
biotreatment plant sludge	1.2 kg	ND	15,350	ND	ND	ND	320	ND	15,670	19,000	0.135
TOTAL										140,497	

ND: Not determined; NTD: Not detected; NA: Either concentration or MATE value not available
a: For concentration ranges, the median was used
b: Relative Hazard = Total hazard units per Mg coal/140,497

7.0 PREFERRED TECHNOLOGY AND PROBLEMS OUTSTANDING

7.1 INTRODUCTION

Three topics appear to deserve mention in this section:

1. Vents from storage tanks and vessels,
2. Naphthalene handling and final coolers, and
3. Cyanide handling.

This discussion is qualitative, as the data are insufficient to support a solid quantitative discussion.

It should be mentioned here that Dunlop and McMichael[47] have discussed in detail one approach to determining optimum treatment methods for a coke plant. Dunlop and McMichael concluded that overall, wastewater quenching was better than wastewater discharge regardless of treatment level. In addition, they concluded that some treatment levels produced adverse overall results. The reader should refer to the cited paper[47] for the complete discussion.

Vents from Tanks and Process Vessels

A large proportion of the emissions from a by-product plant originate in the various vents in the plant. Recovery of vapor from these sources will generally be complicated by the presence of naphthalene. Wilputte Corporation[19] has installed water sprays on some tar decanters, and the techniques might be extended to other vents. Vapor recovery from these sources to the suction side of the exhausters, probably ahead of the primary coolers, might be possible. Naphthalene condensation would require that the vents be heated, and the corrosive nature of the vapor (perhaps including chlorides) would cause materials problems. The system might be designed to float on coke oven gas at slightly above atmospheric pressure.

Naphthalene and Final Coolers

Naphthalene collection in open vessels inherently causes naphthalene emissions. Avoidance of exposed naphthalene by the use of a tar bottom final cooler and keeping the naphthalene in the tar are proven and should be preferable. A wash oil final cooler also collects naphthalene, but the naphthalene must eventually be removed from the wash oil. The final cooler cooling tower with a tar bottom final cooler would still have about the same level of cyanide emissions, although hydrocarbons emissions might be down. A wash oil final cooler should avoid the cyanide emissions, although the cyanide must go somewhere.

Cyanide Handling

A significant proportion of the cyanide is collected in the ammonia liquor, and some is stripped out in the ammonia stills. Essentially all could be stripped from the liquor. The final cooler will collect some and it may be emitted in the cooling tower. Cyanide in the gas will complicate life for a desulfurization unit. The point is that the complete cyanide distribution must be considered before one can be comfortable with any particular treatment scheme.

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APPENDIX A

SAMPLING AND ANALYSIS PROGRAM

APPENDIX A

SAMPLING AND ANALYSIS PROGRAM

DESCRIPTION OF BY-PRODUCT PLANT SAMPLED

A flow plan of the coke by-product recovery plant at which the sampling was done (Fairfield Works, U.S. Steel Corporation) is presented as Figure A-1. Salient features are:

- indirect primary coolers with recirculating cooling water;
- scrubber type tar extractors;
- saturated ammonium sulfate crystallizers with centrifugal dewatering;
- contact recirculating water final cooler with froth flotation naphthalene separator and integral cooling tower;
- naphthalene dried by steam heating;
- light oil recovery in multiple scrubbers and rectification to secondary light oil and the light oil stream;
- no desulfurization;
- flash distillation of tar into chemical oil and pitch;

Further descriptive information is provided where appropriate in the work-up of individual samples and emission rates.

SAMPLING

The sampling and analysis performed during this project was based on the EPA Level 1 protocol.[58] The Level 1 protocol recommends that all identified emissions to all media be sampled and analyzed, as well as the feeds to and products of the process. Level 1 samples are short-term integrated samples for the gases, and grab samples for solids and liquids. The Source Assessment Sampling System (SASS) is the primary sampling apparatus for gaseous samples. The SASS consists of a heated probe, three cyclones and a filter to collect and size particulate (all enclosed in an oven), an adsorbant

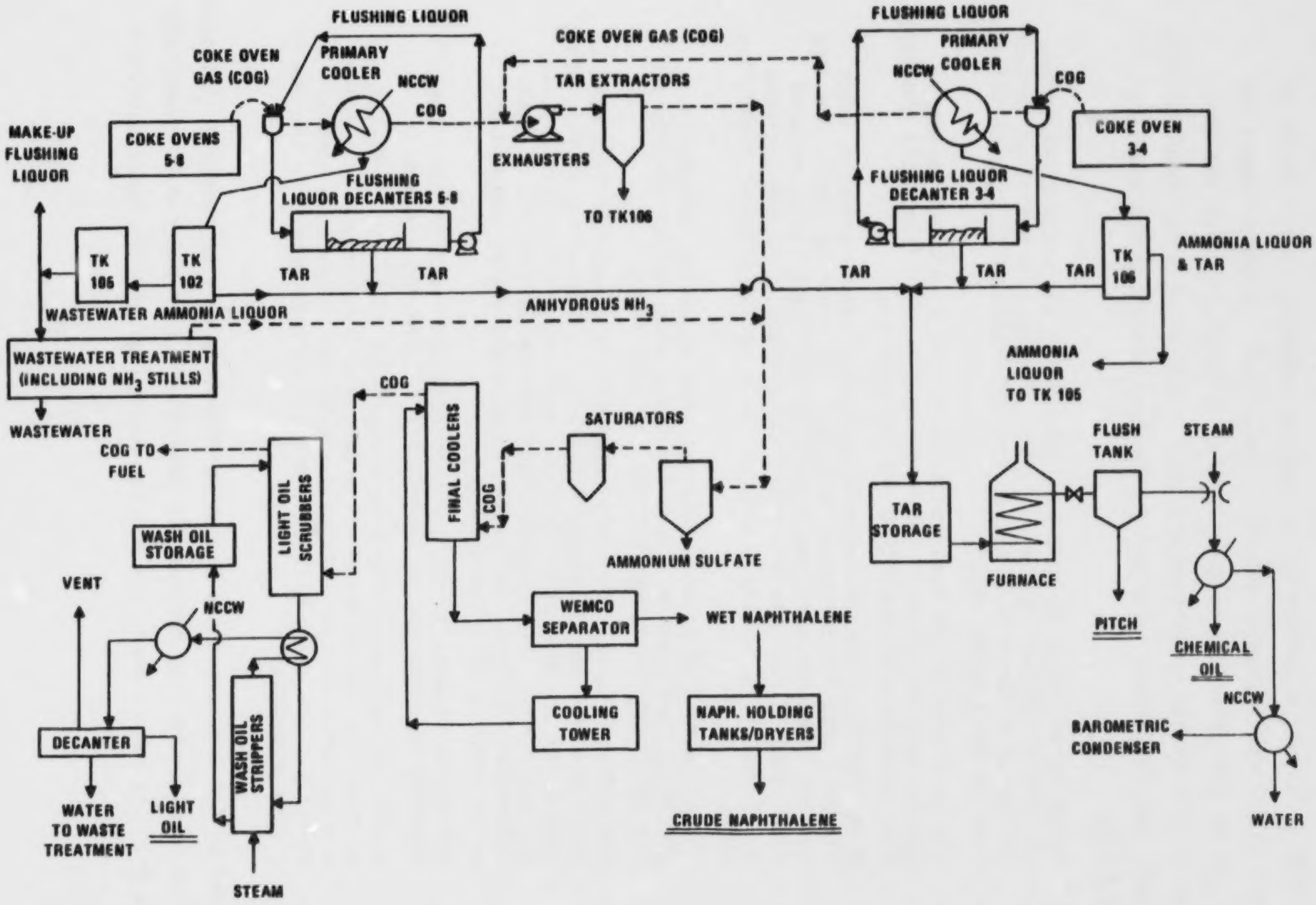
FLUSHING LIQUOR
COKE OVEN GAS (COG)
PRIMARY COOLER
NCCW
COG
COKE OVENS 5-8
MAKE-UP FLUSHING LIQUOR
FLUSHING LIQUOR DECANTERS 5-8
TK 105
TK 102
TAR
TAR
WASTEWATER AMMONIA LIQUOR
WASTEWATER TREATMENT (INCLUDING NH3 STILLS)
WASTEWATER
COKE OVEN GAS (COG)
TAR EXTRACTORS
EXHAUSTERS
TO TK106
ANHYDROUS NH3
FLUSHING LIQUOR
PRIMARY COOLER
NCCW
COG
COKE OVEN 3-4
FLUSHING LIQUOR DECANTER 3-4
TAR
TAR
TAR
TK 106
AMMONIA LIQUOR & TAR
AMMONIA LIQUOR TO TK 105
COG
COG TO FUEL
LIGHT OIL SCRUBBERS
WASH OIL STORAGE
VENT
NCCW
DECANTER
WATER TO WASTE TREATMENT
LIGHT OIL
WASH OIL STRIPPERS
STEAM
FINAL COOLERS
COG
SATURATORS
AMMONIUM SULFATE
WEMCO SEPARATOR
WET NAPHTHALENE
COOLING TOWER
NAPH. HOLDING TANKS/DRYERS
CRUDE NAPHTHALENE
TAR STORAGE
FURNACE
FLUSH TANK
PITCH
STEAM
CHEMICAL OIL
NCCW
BAROMETRIC CONDENSER
WATER

Figure A-1. Flow diagram: Coke by-product recovery plant at USS Fairfield works.

module (XAD-2 resin) to collect C_7 and heavier organics, and a series of impingers to collect inorganic vapors. Light (C_1-C_7) organic vapors and sulfur species are collected as grab samples using glass bulbs and are analyzed on-site by gas chromatography (GC). Samples were collected at only one plant. Considerations important in the development of the sampling program follow:

1. There is an extensive data base concerning the process operations at coke by-product recovery plants. The data do not often include effluents or emissions, but do provide important background information on the process itself.
2. The proximity of the coke batteries to the by-product recovery plants made isolation of the by-product plant a formidable challenge, particularly with respect to ambient sampling.
3. Most sampling locations were in explosion hazard areas in which standard SASS train heaters and pumps could not be used. The long suction lines between sample canister and pumps led to reduced flow rates if the complete train was operated. As the cyclones and filter were not used, samples could be collected at reasonable rates.
4. The pollutants of primary interest were aromatics, polycyclic aromatics, and cyanide. Specific tests were run for cyanide and the adsorbant module was run for the SASS train.
5. The Effluent Guidelines Division of EPA is sponsoring test work on wastewater streams at by-product plants, and sampling at this plant took place the week prior to RTI's sampling visit. This work was not duplicated. The subject plant considered portions of their wastewater treatment facilities to be proprietary, and did not allow sampling at those points.
6. One desired sample point, the noncondensable vent in the light oil recovery process, was not accessible and was not sampled.
7. Nearly all emissions from a coke byproduct plant are fugitive and at rates too low to measure. Under this restriction, only major storage tanks or tanks with measurable vent rates were sampled directly. Explosion hazards limited flow measurement to the use of a vane anemometer.

Based on the considerations discussed above, as well as resource limitations, a modified Level 1 sampling program was developed. This program is summarized in Table A-1. As can be seen, the program emphasizes organic vapor emissions.

TABLE A-1. SAMPLING PROGRAM—BY-PRODUCT PLANT ASSESSMENT

Sample	Date	Gas Grab Sample		Liquid Grab Sample	Solid Grab Sample	NaOH Bubblers	SASS Organic Module	Emission Rate	Comments
		Glass Bulb	Evac Canister						
Naphthalene Flotation Separator	12/12/77	X	X				X	Unknown	
Final Cooler Cooling Tower	12/13/77	X	X	X		X	X	--	Got liquid samples from hot well & cold well
Tar Storage Tank	12/13/77	X	X				X	See comment	Calculated from breathing loss equation
Tar Decanter	12/14/77	X	X				X	See comment	Calculated from breathing loss equation
Light Oil Tank	12/14/77	X	X						
Naphthalene Drying Tank	12/15/77								Bulbs extracted and analyzed
Chemical Oil Tank	12/15/77	X	X				X	See comment	Calculated from breathing loss equation
Excess Ammonia Liquor	12/14/77			X					
Coke Oven Gas	12/14/77	X	X						
Sludge-WWTP	12/15/77				X				
Ambient Upwind	12/16/77	X	X				X		
Ambient Downwind	12/16/77	X	X				X		
24-hr Integrated Ambient Samples	12/12-12/16/77					X			
Ammonia Flushing Liquor Tank	12/16/77	X	X						

Six types of samples were collected during the visit, and these are discussed below. Specific sample data sheets and work-ups are presented later in this appendix.

Gas Bulbs

The gas bulb sampling technique used was to purge at least three bulb volumes through the bulb and collect the fourth. Either a squeeze bulb or mechanical pump was used. The bulbs were 500 ml glass with Teflon® stopcocks. Two bulbs were filled at most sample sites for the on-site gas chromatograph analysis for lower boiling (<100° C) hydrocarbons.

Stainless Canisters

Grab samples of vapor were also collected in evacuated stainless steel cans for more extensive analysis of aromatics at RTI. The cans were approximately one liter in volume, evacuated to about 1 millibar absolute pressure. The cans were connected to the purged probe used for the gas samples and the valve opened to draw in the samples.

XAD-2 Resin Module

Samples of C_7-C_{12} organics were collected in the SASS train XAD-2 module. The probe and cyclones from the SASS train were not used. The probe used was a 13 mm (0.5 in.) Teflon® tube encased in a larger hose for protection. The probe was 10 feet long and connected directly to the SASS organic module. The SASS impinger train was used with the specified solutions, but the solutions have not been analyzed. The circulating cooling water systems could not be used without electricity, so cooling was provided by manual addition of ice to the impinger bath and cooling water well in the organic module. As the samples were generally at ambient temperature, this was not a serious handicap. The XAD-2 resin was prepared and the canister filled per Level 1 protocol. SASS run length varied from 1 to 4 hours, or 5.64 m^3 to 28.64 m^3 (200 to 1,011 ft^3) at standard conditions. Run volume was a nominal 28.00 m^3 or a measured 10 percent mass loading of benzene and homologs on the XAD-2 resin as determined by the aromatics concentration measured by on-site gas chromatography. Use of the SASS gave the XAD-2 resin samples, rinses of the resin modules, and in one case an aqueous condensate.

Liquid and Solid Samples

Liquid samples were collected as grab samples into amber glass bottles as specified in the Level 1 Procedures Manual, as was the sludge sample.

Cyanide in Gas

Sampling specifically for cyanide was done with sodium hydroxide bubblers. The bubbler containers held 60 ml of 0.5 m sodium hydroxide. Ambient samples were collected for 24 hours, from 3:00 p.m. of one day to 3:00 p.m. of the next. The ambient sample rate was 10 l/hr. The final cooler cooling tower sample collected at 60 l/hr for a total volume of 21 liters.

ANALYSIS PROCEDURES

Overview of Level 1 Organic Analysis Methodology

An overview of the methodology used for the Level 1 organic analysis is shown in Figure A-2. This methodology deals with the preparation of the samples to provide a form suitable for analysis, and with their subsequent analysis.

As indicated in Figure A-2, the extent of the sample preparation required varies with sample type. The low molecular weight, volatile species (C_1-C_7 or boiling point <110° C) are determined by gas chromatography on site and require no preparation. The majority of the samples, including the SASS train components, aqueous solutions and bulk solids require extraction with solvent prior to analysis. This extraction separates the organic portion of the samples from the inorganic species. The analysis of organic extracts or organic liquids then proceeds to initial quantitative analyses of volatile (total chromatographable organics, TCO) and nonvolatile (gravimetric, (GRAV) organic material and a preliminary infrared (IR) spectral analysis. The IR spectrum provides an indication of the types of functional groups present in the GRAV sample.

The sample extract or organic liquid is separated by silica gel liquid chromatography (LC), using a solvent gradient series, into seven fractions of varying polarity. TCO and gravimetric analyses of each fraction are done to determine the distribution of the sample by the various class types. An IR

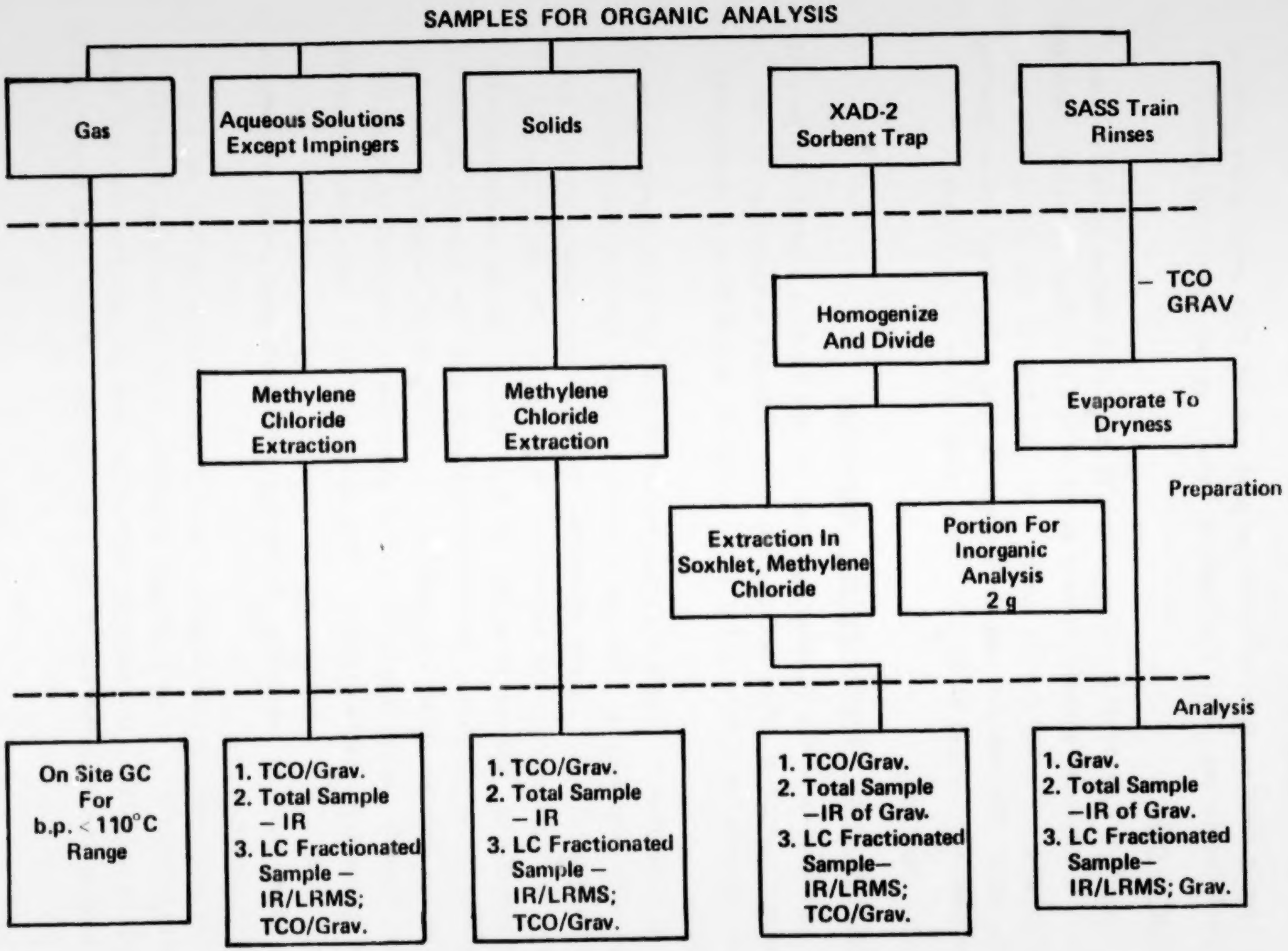
SAMPLES FOR ORGANIC ANALYSIS
Gas
Aqueous Solutions Except Impingers
Solids
XAD-2 Sorbent Trap
SASS Train Rinses
– TCO GRAV
Homogenize And Divide
Methylene Chloride Extraction
Methylene Chloride Extraction
Evaporate To Dryness
Preparation
Extraction In Soxhlet, Methylene Chloride
Portion For Inorganic Analysis 2 g
Analysis
On Site GC For b.p. < 110°C Range
1. TCO/Grav.
2. Total Sample – IR
3. LC Fractionated Sample – IR/LRMS; TCO/Grav.
1. TCO/Grav.
2. Total Sample – IR
3. LC Fractionated Sample – IR/LRMS; TCO/Grav.
1. TCO/Grav.
2. Total Sample –IR of Grav.
3. LC Fractionated Sample– IR/LRMS; TCO/Grav.
1. Grav.
2. Total Sample –IR of Grav.
3. LC Fractionated Sample– IR/LRMS; Grav.

Figure A-2. Organic analysis flowsheet – Level 1 Methodology.

spectrum is then obtained on the GRAV portion of each LC fraction for determination of the types of functional groups present. A low resolution mass spectrum (LRMS) is prescribed for all fractions which exceed the concentration threshold in order to determine the principal compound types present in each fraction. For the sample streams identified in the Level 1 scheme, these concentration thresholds are:

- Gas streams sampled with the SASS system -- 0.5 mg/m^3 computed at the source or 15 mg per LC fraction for a 30 m^3 sample.
- Liquid or solid streams -- 1 mg/Kg extracted or 1 mg per LC fraction, whichever was larger.

The decision is based on the sum of the TCO and GRAV analysis for each fraction. Unfortunately, problems in the analysis procedure, discussed further below, prevented successful LRMS of many samples.

On-site GC Analysis of Gas Samples

The on-site GC analysis was based on the EPA Level 1 methodology, with some variations in instrument conditions where required to improve performance.

As described above, grab samples were collected by flushing a 500 ml glass sampling bulb with the sample gas. Samples were removed from the bulb with a 10 ml Pressure-Lok® gas tight syringe and then injected into the appropriate six port sampling valve equipped with a 1 ml sample loop.

The low molecular weight C_1-C_7 hydrocarbons and benzene were quantitated using the conditions given below:

Column:	Durapak N-Octane, in S.S. 1/8" x 190.5 cm; conditioned at 120° C overnight
Detector:	Flame Ionization
Temperature Program:	Isothermal at 30° C for 4 minutes 30°-100° C at 4°/minute Hold at 100° C until cleared
Helium Flow Rate:	20 ml/min

To minimize adsorption on the sampler surfaces during the quantitation of the sulfur species, the sampling valve used was constructed of Carpenter-20 steel (a high nickel content alloy), the sample lines as well as the column itself were FEP Teflon tubing and the interface between the column and the detector was replaced with glass-lined stainless steel tubing. In addition, the sampling valve was mounted inside the column oven and maintained at the temperature of the column.

The conditions for the sulfur analyses are given below:

Column: Polyphenylether on Chromosorb T; 36' x 1/8" Teflon tube; conditioned at 100° C overnight

Detector: Flame photometric

Temperature Program: Isothermal @60° C

Helium Flow Rate: 20 ml/min

For the GC analysis of permanent gases, all columns, restrictors, and valves were enclosed in a single valve oven to minimize space requirements and to insure that all components were heated to the same isothermal temperature. The conditions for the permanent gas analysis are given below:

Column: Molecular sieve 5A, 6' x 1/8" S.S. and Porapak N, 8' x 1/8" S.S. with column switching

Detector: Thermal conductivity

Temperature Program: Isothermal at 100° C

Carrier Flowrate: 30 ml/min

Analysis of Evacuated Canister Gas Samples

Grab samples were also collected in specially designed and prepared 2-liter stainless steel sampling containers. These containers were evacuated and shipped to the field.

Samples were collected by attaching a sampling probe and momentarily opening the shut-off valve until atmospheric pressure was reached. The containers were returned to the RTI labs for the subsequent analysis of benzene and substituted benzene compounds. Samples were removed from the containers using an in-house designed and built sampling device which utilized a Heise gauge and the principle of pressure differentiation. The conditions for the analysis are given below:

Column: 10%, 1,2,3-tris(2-cyanoethoxy) propane on 100/120 mesh Chromosorb PAW, 8' x 1/8" S.S.
Detector: Flame Ionization
Temperature Program: Isothermal at 80° C
Helium Flow Rate: 20 ml/min

Calibration for the analyses was peformed initially on all compounds, (C_1 through C_7 normal parafins, benzene and homologs, and sulfurs) to determine their retention time and area count. Subsequent calibration was performed daily by checking the retention time and area count of methane, benzene, and sulfurs only.

Preparation of Sample Extracts

Aqueous Solutions--

Extraction of aqueous solutions was carried out with methylene chloride using a standard separatory funnel fitted with a ground glass stopcock (no grease was used). The pH of the aqueous phase was adjusted first to 2.0 ± 0.5 with hydrochloric acid and subsequently to 12.0 ± 0.5 with sodium hydroxide, using multi-range pH paper for indication. Two extractions were done at each pH, using a 500-ml portion of methylene chloride for each of the four extractions of an approximately 10-liter sample.

For the SASS train sorbent module condensate, the volume of aqueous solution was measured and the quantity of methylene chloride adjusted proportionately. The extractions were done on-site to avoid the necessity of shipping large quantities of water.

Solids--

The sludge sample was extracted for 24 hours with methylene chloride in a Soxhlet apparatus. The Soxhlet thimble was glass with an extra coarse fritted disc and was previously extracted in order to avoid contamination. The sample is covered with a plug of glass wool during the extraction to avoid carryover of the sample. Solids separation was difficult to achieve with this biological plant sludge.

Sorbent Trap--

The XAD-2 resin from the sorbent trap was removed from the SASS train cartridge in the field and stored in an amber glass bottle with a Teflon® top liner. At RTI, the resin was homogenized, and a 2-g portion removed for the inorganic analysis. The inorganic analysis was not run as part of this study, although the sample is being retained. The balance of the resin (about 130 grams) was extracted with methylene chloride to remove the organic material in a large Soxhlet extraction apparatus. The resin was transferred to a previously cleaned glass extraction thimble and secured with a glass wool plug. Approximately 2 liters of methylene chloride were added to the 3-liter reflux flask. The resin was extracted for 24 hours. The boiling solvent in the flask was examined periodically to determine whether additional methylene chloride was needed to replace that lost by volatization.

SASS Train Rinses--

For each SASS train run there was a sample from the rinse of the sorbent module. The solvent mixture for this rinse was 1:1 (v:v) methylene chloride: methanol. The SASS sorbent module rinses were analyzed for TCO prior to concentration. Then the rinses were dried to constant weight by nitrogen blowing at ambient conditions to remove the methanol solvent prior to LC separation.

Analysis of Samples of Organics C_8 to C_{16}

The analysis of each of the prepared or isolated samples for organic compounds followed the scheme introduced in Figure A-2.

Quantitative analysis of moderately volatile materials (b.p. 100° C-300° C equivalent to the C_8 to C_{16} normal hydrocarbon range) was achieved by a gas chromatographic procedure (TCO) applied to various organic solvent extracts, liquids, and SASS sorbent module rinses. Nonvolatile organic sample components (b.p. >300° C) were measured by evaporating an aliquot of the extract to dryness and weighing the residue (GRAV procedure).

In summary, a TCO analysis of each extract, organic liquid, and sorbent module rinse was performed prior to any concentration step. It was then necessary to do a gravimetric analysis on an aliquot of the extract, to obtain an IR on the GRAV portion from this extract, and to concentrate the extract for the LC separation. The appropriate stage at which to conduct each of these steps (gravimetric analysis, IR, concentrate) depended on the quantity and solubility of the sample. For all samples, quantitative analyses (TCO and GRAV) were required both before and after concentration.

Total Chromatographable Organics (TCO)--

Samples supplied for TCO analysis were in the liquid form originating either as a SASS rinse or an extract. Generally, nine separate TCO analyses were performed on each sample; a preliminary, a concentrate, and 7 LC fractions. This excludes the standard which was verified daily and numerous blanks corresponding to the 9 analyses per sample. The standard mixture was prepared in methylene·chloride using the normal alkanes, octane, dodecane, and hexadecane. The concentration of the standard was typically in the range of 5-10 mg/ml representing the combined weight of all compounds per ml. Typically, 1.5 to 2 µl of all samples were injected onto the column with peak integration covering only the time span between the retention times of n-heptane and n-heptadecane. The results were reported as a total weight of organic material after the appropriate blank value had been subtracted. The analyses were performed using the conditions given below:

Column:	10% OV-101 on 100/120 mesh Supelcoport 6' x 1/8" S.S.
Detector:	Flame Ionization
Temperature Program:	Isothermal @30° C for 4 minutes 30°-250° C @16° /min 250° C until cleared
Helium Flow Rate:	20 ml/min

Gravimetric (GRAV) Analysis--

The Level 1 GRAV analysis is used to quantitate the highest boiling (roughly greater than 300° C) organic compounds collected by the sampling procedure. The GRAV residue is also the portion of the sample on which an IR spectrum is obtained. Where possible, at least 10 mg of sample was weighed in a GRAV analysis. Weighing was to a precision of ± 0.1 mg. Level 1 procedures require that not more than 5 ml of the sample extract or one-half the total sample, whichever is smaller, be subjected to GRAV analysis.

The procedure used to dry the GRAV samples is described below:

1. Label vials with permanent marker and desiccate for 20 hours. Caps not desiccated.
2. Allow vials to stand exposed to air for 4 hours.
3. Weigh vial and cap together.
4. Add sample aliquot and blow down with dry $N_2(g)$.
5. Desiccate 20 hours (vials only) and again weigh vials and caps.
6. Repeat above procedure two additional times or until change in weight is ± 0.1 mg.

Preliminary Versus Concentrate Data--

GRAV and TCO analyses were performed on both the original sample (preliminary) and on the concentrated sample. In most cases the TCO data were fairly consistent between the preliminary and concentrated samples--the TCO mass of the concentrate was 70 to 140 percent of that in the original sample, with an average of 90 percent. Considerably more variation existed between the GRAV of the concentrated sample and that of the original sample. The error cannot be conclusively attributed to any single source. As the original samples often had only a few tenths of a milligram of GRAV material in the aliquot which was taken to dryness, the use of a balance with a 0.1 mg precision (as prescribed by the Level 1 procedure) introduced some error (tare weight of the vials was around 2.7 g). In addition, the fact that some samples had not achieved constant weight after 3 days desiccation and blowing down with N_2 indicates problems in the determination of GRAVs to within a few milligrams. GRAV determinations for the concentrated samples were made on larger masses and thus suffer less from balance error.

Liquid Chromatographic (LC) Separation--

All sample extracts, neat organic liquids, and SASS train rinse residues (after drying to remove methanol) were subjected to LC separation if sample quantity was adequate. A 100 mg portion of the sample was preferred for the

LC, but smaller quantities down to a lower limit of about 15 mg were allowed. The sample was separated into compound classes on silica gel using a gradient elution technique. The column and adsorbent were as described below:

Column: 200 mm x 10.5 mm ID, glass with Teflon® stopcock, water-jacketed with inlet water temperature in the range of 18°-22° C.

Adsorbent: Davison, Silica Gel, 60-200 mesh, Grade 950 (Fisher Scientific Company). This adsorbent was activated at 110° C for at least two hours just prior to use, and cooled in a desiccator. No preclaiming was required by the Level 1 protocol.

Table A-2 shows the sequence for the chromatographic elution. In order to ensure adequate resolution and reproducibility, the column elution rate was maintained at 1 ml per minute.

TABLE A-2. LIQUID CHROMATOGRAPHY ELUTION SEQUENCE

Fraction	Solvent Composition	Volume
1	Pentane	25 ml
2	20% Methylene chloride in pentane	10 ml
3	50% Methylene chloride in pentane	10 ml
4	Methylene chloride	10 ml
5	5% Methanol in methylene chloride	10 ml
6	20% Methanol in methylene chloride	10 ml
7	50% Methanol in methylene chloride	10 ml

EPA Level 1 procedures were followed for the LC work. A bank of 4 LC columns allowed the use of a single solvent blank for each 3 samples. In many cases the GRAV mass of the blanks was significant. GRAV mass for the LC cuts is given both before and after subtraction of the blank mass. The silica gel was apparently the source of the spurious GRAV mass.

Spectroscopy--

Infrared (IR) analysis of the total sample (preliminary), concentrate, and LC cuts was performed on the GRAV residue whenever there was adequate sample mass. The instrumentation used was a Nicolet Model 7199 Fourier Transform IR, which allowed resolution beyond that required by the Level 1 protocol. Samples which were below the Level 1 criteria for IR work by organic mass, but on which IR spectrum were obtained are so indicated. The GRAV residue was dissolved in methylene chloride, placed on a KBr salt plate, and allowed to dry before running. The spectra were interpreted and the results and data sheets are included in this appendix.

Low resolution mass spectroscopy (LRMS) was used on the samples when indicated by sample quantity per the Level 1 protocol. Problems were encountered with the LRMS due to interference from the solvents and inability to perform solvent exchange without losing significant amounts of TCO material.

Level 1 protocol stipulates that, for LC samples with greater than 2 mg of TCO material when referenced back to the source, LRMS analysis be carried out using the batch inlet. Some question regarding the efficacy of this approach were raised because of the overwhelming quantities of solvent (methylene chloride) molecules present compared to solute molecules. Liquid chromatographic fraction Number 6 of the XAD-2 module rinse for the chemical oil tank was analyzed using the batch inlet system. No peaks other than those associated with methylene chloride were present. The solution was concentrated by a factor of 2.5 and analyzed again. Aside from methylene chloride, 3-4 additional components were noted. Further concentration by a factor of 2 followed by a batch inlet run produced a spectrum with 4-5 compounds other than methylene chloride. Further concentration is of dubious value since TCO material is too readily lost.

This approach, i.e., the detection of small amounts of solute in the presence of gross amounts of solvent, is being reexamined at RTI under a separate EPA contract to determine the concentration levels at which known amounts of known semi-volatile materials can be adequately detected. With this information the criterion for LRMS analysis of TCO material via the batch inlet may be altered. For this reason the samples analyzed under this contract that meet the Level 1 TCO LRMS criterion (some 60 samples) have not yet been analyzed. These samples have been stored. LRMS work that did not suffer from this interference problem was completed and the results are included in this appendix.

Gas chromatography/high resolution mass spectroscopy (GC/MS) work was done on three samples to check for the presence of high molecular weight PNA's in the vapor samples. The instrumentation was an LKB Model #2091

GC/MS. The column used was a 1 percent SE 30/barium carbonate wall coated open tubular column (WCOT) 16.8 m long. Following injection, the column temperature was held at 70° C (100° C in one case) for 2 minutes, then advanced at 8° C per minute to 240° C. The scan rate for the GC/MS was 2 seconds per scan over the range from 50 mass units to 490 mass units. Limits of detectability for polynuclear aromatics was in the range of 15-100 µg/µl, which for these samples was 16-106 weight parts per billion (wppb) for the tar decanter, 2.4-16 wppb for the tar storage vapor, and 0.01-0.06 wppb for the final cooler cooling tower. The above calculations assumed a compound with a molecular weight of 250.

Analysis for Cyanide--

The method used to determine the cyanide concentrations in the NaOH bubblers was a titrimetric procedure[67] using silver nitrate and a silver sensitive indicator (p-dimethylamino-benzal-rhodamine).

Work-Up and Presentation of Data--

The data collected during this test work are presented in several different formats depending on the type of sampling and analysis utilized. The bulk of the results are from the Level 1 analyses, including the C_1-C_7 on-site GC work, the analysis of the XAD-2 module sample and the GC work for aromatics identification. Samples collected at the froth flotation separator, final cooler cooling tower, tar storage tank, tar decanter, light oil tank, chemical oil tank, and from the ambient air are all treated in essentially the same way. The first data sheet presented for a given emission source is the SASS data sheet. The second data sheet presents the results of the GC analyses, both on- and offsite, Level 1 as well as specific compound quantitation. The third table presented is the organic extract summary, a work-up of the Level 1 data. At the top of the table is the total organics concentration (sum of the original sample TCO and GRAV divided by the SASS sample volume). The GRAV and TCO analyses were rationed back to the original extract on a volumetric basis:

$$\begin{array}{c}\text{GRAV or TCO in}\\ \text{original extract}\end{array} = \begin{array}{c}\text{GRAV or TCO}\\ \text{measured in aliquot}\end{array} \times \frac{\text{Volume of Extract}}{\text{Volume of Aliquot}}$$

The next two lines of the table present the TCO and GRAV masses, respectively, ratioed back to the total sample for the preliminary, concentrate, and GC cuts. The GRAV and TCO values are on a net basis, the blanks having been subtracted (negative weights are reported as zero in this table).

In a few cases the GRAV mass after subtraction of blanks was zero for all LC cuts in spite of a significant GRAV mass in the concentrate and preliminary GRAV's. In these cases the GRAV mass before blank subtraction is presented in parentheses in the table.

The complete XAD-2 canister rinse samples were taken to dryness after a preliminary TCO and GRAV analysis. The total sample GRAV then is straightforward--the mass of the dry residue. A portion of the dry residue was weighed, dissolved in a small amount of methylene chloride, and put on the LC column. The GRAV of the LC cut was then ratioed back up to the original sample by the formula:

$$\begin{array}{c}\text{GRAV LC cut mass on total}\\ \text{sample basis}\end{array} = \frac{\text{total GRAV mass}}{\text{GRAV mass put on LC column}} \times \begin{array}{c}\text{GRAV mass}\\ \text{in LC cut}\end{array}$$

The TCO mass was ratioed up on the same basis, although the fact that the sample had been dried opens the question of what fraction of the TCO had been lost.

The remainder of the table is devoted to interpretation of the Level 1 LC and IR results. The basic quantity used in this interpretation is the MATE (minimum acute toxicity concentration) Comparison Value, a synthetic number with concentration units (mg/sm^3). The intent of this portion of the table is to present a structured and uniform (with respect to the other samples) interpretation of this part of the Level 1 analysis. MATE Comparison Values were only prepared for streams discharged to the environment. Thus, excess ammonia liquor and the final cooler liquid sample are not so treated. MATE Comparison Values were calculated as follows:

1. The GRAV mass for a given LC fraction was ratioed back to the original sample and divided by the SASS sample volume to obtain the GRAV concentration for the LC fraction.
2. The IR spectrum interpretation for the given LC cut was then evaluated in the light of the compound classes expected in the LC cut based on work presented by Harris[59] as shown below:

aliphatic hydrocarbons	LC cut 1
halogenated aliphatics	LC cut 1
aromatic hydrocarbons	LC cuts 2, 3 or 4
halogenated aromatics	LC cuts 2, 3 or 4
heterocyclic N, O, S compounds	LC cuts 4 or 5
sulfides, disulfides	LC cuts 4 or 5
nitriles	LC cuts 4 or 5
ethers	LC cuts 4 or 5
aldehydes, ketones	LC cuts 5 or 6
nitroaromatics	LC cuts 5 or 6
alcohols	LC cuts 5 or 6
amines	LC cuts 5 or 6
phenols; halo and nitrophenols	LC cuts 6 or 7
esters, amides	LC cuts 6 or 7
mercaptans	LC cuts 6 or 7
carboxylic acids	LC cuts 6 or 7
sulfoxides	LC cuts 6 or 7

A compound type which was identified in the IR spectrum of an LC cut was entered in the Summary Table as having a MATE Comparison Value equal to the total GRAV concentration for that fraction. Compound classes which would be expected in an LC cut if present, but not indicated by IR, were entered in the table at 10 percent of the total GRAV concentration. This procedure is a modified version of that presented by Harris.[59]

The MATE Comparison Values then are not emission factors for a compound class, and for a given LC cut total more than the GRAV mass of that LC cut. They do, however, assist in the comparison of various sources within the by-product plant. The reader should note that TCO mass is not included in this procedure, as the TCO material was not present in the samples analyzed by IR or if TCO was present it was included in the GRAV mass reported. For several sources, TCO material is the majority of the organics present.

The chosen compound classes generally follow the classification scheme used in the Multimedia Environmental Goals (MEG's) list.[60]

The other data sheets for a given source are the IR interpretation sheets and, where applicable, the LRMS interpretation. The analyses are arranged with the preliminary IR first, followed by the concentrate and then the LC cuts.

INDIVIDUAL SAMPLES AND WORK-UP

Froth Flotation Separator

Naphthalene collected in the final cooler was separated in a froth flotation chamber. The separator was a WEMCO design, roughly 25 feet long, 10 feet wide, and 10 feet deep. Hatches, presumably for cleaning, were present in the top. The sample was taken by placing the probe in the vapor space through one of the hatches and closing the hatch over it. No measurable emission was present from the separator.

The samples collected at the separator were two glass bulbs, an evacuated cylinder, and a SASS organic module. The SASS run collected 28.6 sm^3 (1010 scf) of vapor at a temperature of 12° C at the XAD-2 resin. Tables A-3 through A-24 are the complete data sheets and analysis work-ups on this sample.

Final Cooler Cooling Tower

The gas and vapor in the airstream directly above the final cooler cooling tower were sampled. All the Level 1 samples were collected using a 30-foot Teflon® probe suspended above the tower. Two glass bulb grab samples, an evacuated canister and a SASS XAD-2 resin sample were collected for hydrocarbon analysis. The XAD-2 resin was exposed to 27.6 sm^3 (975 scf). The temperature at the XAD-2 resin was 14° C.

Sampling for cyanide in the gas was conducted at this site. A 0.64 cm Teflon® line was suspended above one cell of the cooling tower as above and the cyanide collected in 0.5 m sodium hydroxide bubblers. Around 0.02 m^3 gas was sampled in each of two runs.

The design gas rate for the cooling tower was not available. The water rate was known, and the gas rate was estimated to be equal on a mass basis.[68] On this basis, the gas flow rate was 3,230 sm^3/Mg coke (104,000 scf/ton).

Sample and analysis data sheets are presented as Tables A-25 through A-42.

Liquid samples were collected from both the hot and cold wells of the cooling tower. These were grab samples, extracted on-site per Level 1 procedures. Analysis of the sample produced the results given in Tables A-43 through A-85.

Tar Storage Tank

The coal tar storage tanks at the sampled plant were maintained at around 90° C. A total of five tanks function for tar storage, one 250,000 gal, one 500,000 gal, and three 1,000,000 gal tanks. All are cylindrical tanks with cone roofs; with one exception diameter to height is approximately

1:1. Ventilation slots were cut around the sides of the tanks just under the roof junction. A vent was also provided at the top of the cone.

Tar was pumped first to the tank which was sampled, and water (10 percent by volume) was decanted from this tank. The "dry" tar was then stored in a second tank. The other two large tanks were not in use, although they were used at times. The small tank (250,000 gal) was used for storage at the pitch plant.

"Working" losses from these tanks were estimated for filling the various tanks in order as the tar production was moved from place to place; a given volume of tar was pumped to three tanks. During the week we sampled, tar production averaged 46.3 l/Mg coke (11.1 gal/ton coke), so working losses from the three transfers were about 0.14 sm^3/Mg coke (4.5 scf/ton coke).

Breathing loss for these tanks could not be estimated, both because of a lack of basic data (vapor pressure of the tar/water mixture) and the ventilation slits around the tank which allow wind to blow through the tank. The available correlations are not adequate for this purpose.

The sampling was done through a hatch in the top of the tank. The probe was simply lowered about 2 m into the tank, around a meter below the ventilation slits. Glass bulbs, an evacuated canister, and a SASS run were done at this site. The SASS train plugged with naphthalene after about an hour; the total sample volume was 5.6 m^3 (199 scf); the sampled vapor was at about 30° C, as was the XAD-2 resin.

Results of the analyses are presented in Tables A-86 through A-107.

Tar Decanter Tanks

Three tar decanter tanks were in use at the sampled plant, handling 3,626 l flushing liquor per Mg coke produced (871 gal/ton). Each decanter was vented through standpipes in the roof, some of which had measurable emissions. The emission rates were measured by restricting the vent, and forcing the gas through a vane anemometer. The gas temperatures ranged from 74° to 82° C. The three decanters had a total of 18 vents, eight of which were venting at measurable rates. In addition, one decanter had a poorly sealed hatch which was venting; the rate was estimated to be three times the pipe vent rate on that decanter. The total estimated tar decanter vent emission rate was 2.15 sm^3/Mg coke produced (68.2 scf/ton).

The samples collected were two glass bulbs, one evacuated canister, and a SASS XAD-2 resin sample. The SASS sample was of 8.14 sm^3 (287.4 scf), terminated due to the high aromatics content of the stream. Data and analysis sheets are presented as Tables A-108 through A-149.

Light Oil Storage Tank

Light oil production during the sampling visit averaged 13.7 l/Mg coke (3.3 gal/ton), stored in a single 3,785,000 l (1,000,000 gal) tank of conventional cone roof design. Working loss emissions amount then to an estimated 0.03 sm^3/Mg coke (0.45 scf/ton).

Breathing losses were crudely calculated for a hypothetical light oil with a vapor pressure of 50 mm Hg at storage conditions. As light oil composition was not determined, a better estimate is not possible, and in fact may not be warranted for the quality of the correlation.[69] The estimated loss rate was 18 g light oil/Mg coke (0.035 lbs/ton). At the measured gas concentrations for light oil constituents, this would require an emission rate of 15.6 m^3/Mg coke (500 ft^3/ton). The breathing loss is much more significant than is the working loss.

The samples collected were glass bulbs. A Teflon® probe was lowered about 2 m into the vapor space of the tank and connected to an evacuated canister. A SASS XAD-2 module sample was not collected due to sampling difficulties.

Analysis results from this sample are provided in Table A-150.

Chemical Oil Storage Tank

The volatile product of tar distillation, chemical oil, was stored in two tanks, each 10.2 m (33.5 ft) in diameter and 11.9 m (39 ft) high. The production rate of chemical oil was 23.1 l/Mg (5.6 gal/ton) coke during the sampling visit. Working loss was then 0.024 sm^3/Mg coke (0.75 scf/ton). Breathing loss could not be calculated.

Sampling was done by lowering a probe in through a hatch in the top of the tank. Glass bulbs, an evacuated canister, and a SASS XAD-2 module were collected. Naphthalene condensed in the module and had to be scraped off in order to collect the 14.3 sm^3 sample.

Data sheets and analysis results are presented in Tables A-151 through A-172.

Coke Oven Gas

A sample of coke oven gas downstream of the tar scrubbers but before ammonia removal was collected. Two glass bulbs and an evacuated canister were collected. The results are given in Table A-173.

Primary Cooler Condensate Tank

Condensate from the primary coolers were collected in two tanks, and was then combined and put in a third tank. The most accessible of these tanks was sampled, using a glass bulb and an evacuated canister. The rate of emission was estimated by putting a vane anemometer in the vapor stream. The combined total emission rate from the three tanks was 1.7 sm^3/Mg coke (55.3 scf/ton). The gas temperature leaving the tank was 63° C. The on-site GC analysis of the samples is described in Table A-174.

Naphthalene Drying Emissions

Naphthalene slurry was dewatered by decanting and then heating. The drying tanks included two 41,600 l (11,000 gal) horizontal cylindrical tanks and three 83,200 l (22,000 gal) tanks. Each tank was fitted with steam coils and a vent stack which extended about 5 m (16 ft) above the tank. The naphthalene slurry (60 percent water) was pumped into the tank, and the water allowed to separate. After draining, the steam was turned on and the naphthalene melted.

Drying time was generally 24 to 48 hours. The emission rate was estimated by measuring the rate at which air was being drawn into a hatch of a tank by the chimney effect. The vapor within the tank was sampled by lowering glass bulbs into the tank, allowing them to warm, then aspirating through them as described above. The liquid temperature in the tank was 101° C. For an average drying time of 36 hrs, with 16,600 l of liquid naphthalene in the tank at a production rate of 0.74 l naphthalene/Mg coke (0.18 gal/ton coke), the emission rate was 2.94 sm^3/Mg coke (93.4 scf/ton). The naphthalene concentration in the samples was measured by GC and found to be 533 g/sm^3 vapor. This amounts to 1.56 kg napthalene emitted per Mg coke (3.13 lb/ton).

As this is about twice the total naphthalene production of the plant, the sample taken must not be representative in some way.

Ambient Samples for Cyanide

Ambient bubblers were run for 24 hours on each of 4 days. The data were presented earlier in Section 6 of this report and will not be repeated here. Three sample stations were available, only two of which operated on two days. The data sheets for the four days are attached as Tables A-175 through A-178.

Upwind-Downwind Ambient Organic Sampling

Ambient organic samples were collected both upwind and downwind of the plant. Glass bulbs, evacuated canisters, and SASS XAD-2 modules were collected at both sites. The sampling was conducted sequentially, the downwind sample first, followed by the upwind sample. Data sheets and analysis results are presented in Tables A-179 through A-199.

Ammonia Liquor Samples

Grab samples of excess ammonia liquor were collected and analyzed by Level 1 methodology. The sample was collected just before the liquor entered the wastewater treatment plant. The analysis results are given in Tables A-200 through A-230.

Biological Treatment Plant Sludge

A grab sample of sludge was collected and analyzed for organics and by taking a pH 7 extract and subjecting it to Level 1 analysis. The results on this sample were presented in the body of the report. Tables A-23 through A-240 give the analytical results.

RAW GRAV AND TCO Data

The TCO and GRAV data are presented in Tables A-241 and A-242, respectively. The TCO data for the LC cuts is the total mass in the LC aliquot, the blank having been subtracted. The GRAV mass for the LC cuts presented in Table A-242 is the GRAV mass found in the aliquot from the LC procedure. That is, 25 ml of pentane was the first of the solvents put on the loaded LC column. After the pentane had passed through the silica gel, 10 ml was taken as a GRAV aliquot and the value presented in the table is the GRAV mass in that 10 ml aliquot. The total GRAV mass in the LC sample is then 2.5 times the mass in Table A-242. The other LC cuts are collected with 10 ml of solvent, and 5 ml was taken for GRAV determination. Thus these cuts are ratioed to the total GRAV mass in the LC sample by multiplying by 2.0.

Once the total TCO or GRAV mass in an LC sample is known, the TCO or GRAV in the original sample can be calculated as from the ratio of concentrated sample volume to the volume of sample put on the LC column.

TABLE A-3. FROTH FLOTATION SEPARATOR SAMPLE

Plant Name: United States Steel--Coke By-Product Plant

Location: Birmingham, Alabama

Date: 12/12/77

Test Performed By: F. J. Phoenix, E. E. Stevenson

Run Number: 1

Sampling Location: Wemco Separator

Pre Leak Test: 0.04

Post Leak Test: 0.04

Test Time:

Start: 10:15

Finish: 14:25

Meter Volume (c.f.):

Start: 630.59

Finish: 1680.24

Volume of Gas Sampled: 1049.65 c.f.

1011.29 scf

Average Gas Temperature (°F)

Ambient: 54°

Sampling Location: 54°

XAD-2 Resin: 54°

Meter Box: 85°

Comments:

1. No condensate collected.
2. Sampling performed in one of sixteen 8" x 50" openings in top of separator.

TABLE A-4. FROTH FLOTATION SEPARATOR SAMPLE GC ANALYSIS

Sample Date: 12/12/77

Analysis Date: 12/12/77

C_1-C_7 HYDROCARBONS

Bulb #1

Range		# Peaks	ppm (V/V)
GC	1	1	1425
	2	1	441
	3	4	155
	4	1	0.1
	5	5	13
	6	4	30
	7	0	—

Bulb #2

Range		# Peaks	ppm (V/V)
GC	1	1	1291
	2	1	373
	3	4	132
	4	0	—
	5	2	37
	6	1	212
	7	1	3

AROMATICS (ppm, V/V)

	On-Site		RTI
	Bulb 1	Bulb 2	SS Can
Benzene	1814.8	1612.9	914.7
Toluene	162.9	136.1	82.9
Ethyl Benzene	NA	NA	0.5
m & p Xylene	NA	NA	14.4
o Xylene	NA	NA	3.7

SULFURS (ppm, V/V)

	On-Site	
	Bulb 1	Bulb 2
H_2S (COS)	1504	NA
SO_2	—	NA
CS_2	—	NA

NA = No Analysis.

— = Compound Not Detected.

TABLE A-5. ORGANIC EXTRACT SUMMARY, FROTH FLOTATION SEPARATOR, XAD-2 RESIN

	Preliminary	Concentrate	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total organics mg/sm³	649	474	0.0 (10.9)	419 (423)	7.0 (14)	0.87 (6.1)	42 (47)	0.0 (3.5)	0.0 (7.0)	469 (512)
TCO, mg	18,538	13,175	0.0	12,000	200	25	1,200	0.0	0.0	13,425
GRAV, mg	40	394.5	0.0 (312)	0.0 (100)	0.0 (200)	0.0 (150)	0.0 (150)	0.0 (100)	0.0 (200)	0.0 (1,212)

Category				MATE comparison value, mg/sm³*				
Aliphatic hydrocarbons	(10.9)							0.0 (10.9)
Halogenated aliphatics	(1.1)							0.0 (1.1)
Aromatic hydrocarbons		(3.49)	(7.00)	(5.24)	(5.24)	(3.49)	(7.00)	0.0 (31.5)
Halogenated aromatics		(0.35)	(0.70)	(0.52)				0.0 (1.57)
Heterocyclic N, O, S compounds				(0.52)	(0.52)			0.0 (1.04)
Sulfides, disulfides				(0.52)	(0.52)			0.0 (1.04)
Nitriles				(0.52)	(0.52)			0.0 (1.04)
Ethers		(3.49)	(7.00)	(0.52)	(0.52)	(3.49)	(7.00)	0.0 (22.0)
Aldehydes, ketones	(10.9)		(7.00)	(5.24)	(5.24)	(3.49)	(7.00)	0.0 (38.9)
Nitroaromatics					(0.52)	(0.35)		0.0 (0.87)
Alcohols					(5.24)	(0.35)	(7.00)	0.0 (12.6)
Amines					(0.52)	(0.35)	(0.70)	0.0 (2.09)
Phenols, halo and nitrophenols					(5.24)	(0.35)		0.0 (5.59)
Esters, amides	(10.9)	(3.49)	(7.00)	(5.24)	(5.24)	(3.49)	(7.00)	0.0 (42.4)
Mercaptans						(0.35)	(0.70)	0.0 (1.05)
Carboxylic acids						(0.35)	(0.70)	0.0 (1.05)
Sulfoxides						(0.35)	(0.70)	0.0 (1.05)

NOTE: Values in parentheses are GRAV mass before subtraction of blank. The presence of GRAV mass in the original sample is shown by the Preliminary and Concentrate samples. The MATE Comparison Value is based on the GRAV mass in the LC cut divided by the gas sample volume. For compound classes indicated by IR, the MATE comparison value is 100 percent of the GRAV concentration. For compound classes expected[65] but not identified by IR, the MATE Comparison Value is 10 percent of the GRAV concentration.

TABLE A-6. FROTH FLOTATION SEPARATOR: XAD-2 RESIN, PRELIMINARY IR ANALYSIS

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3054	W	aromatic or olefinic CH stretch
2956, 2926, 2854	S	aliphatic CH stretch
1723	M	ketone or ester
1601	M	conj. olefine and/or aromatic $C\overset{\cdots}{-}C$
1495	W	aromatic $C\overset{\cdots}{-}C$
1454	W	aliphatic CH bend
1262, 1069	W	aromatic ester ϕ-CO-O stretch
78	M	substituted aromatic compds

2. Unassigned weak bands: 1713, 1693, 1182, 1022, 824 cm^{-1}

3. Other remarks:

This sample possesses less mass than that required by Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained, however, since Fourier Transform IR techniques were utilized.

Sample appeared to contain principally aliphatic and aromatic ketones and esters. Also, large peak at 1602 cm^{-1} indicates significant amounts of conjugated olefins.

TABLE A-7. FROTH FLOTATION SEPARATOR, XAD RESIN, IR ON SAMPLE CONCENTRATE

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3072, 3054, 3007	W	aromatic and olefinic CH
1956-1674	W	aromatic overtones/combinations
1592, 1387	W,M	α-substituted naphthalene, or conjugated vinyl $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ stretch
1269-1005	W	aromatic fingerprint region
958	M	vinyl CH bend, or aromatic in-plane bend
782-700	S-M	substituted aromatic compds

2. Unassigned weak bands: 1504, 847, 618 cm^{-1}

3. Other remarks:

Sample contains substituted aromatic and/or unsat. hydrocarbons. Large band at 782 cm^{-1} suggests that sample is predominantly naphthalene, *i.e.*, band at 782 cm^{-1} is the resultant of CH out-of-plane bending of 4 adj. aromatic H.

TABLE A-8. FROTH FLOTATION SEPARATOR, XAD RESIN, LC CUT #1 IR

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2954, 2932, 2856	S	aliphatic CH stretch
1740	M	ester or aliphatic ketone
1459	M	
1438, 1376	W	aliphatic CH bend

2. Unassigned weak bands:

3. Other remarks:

TABLE A-9. FROTH FLOTATION SEPARATOR, XAD RESIN, LC CUT #2 IR

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2958, 2927, 2857	S	aliphatic CH stretch
1741	W	ester
1464, 1378	M,W	aliphatic CH bend
1261	S	ester of aromatic or α,β-unsaturated acids
1078, 1041	S	aliphatic ethers, or esters
863, 749, 702	W	substituted aromatic
802	S	substituted aromatic--predominantly α-substituted naphthalene or m-sub. benzene

2. Unassigned weak bands: 1613, 1604

3. Other remarks:

This sample possessed less mass than that required by bend 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample predominantly esters of aromatic and/or α,β-unsaturated acids and/or aromatic and aliphatic ethers.

TABLE A-10. FROTH FLOTATION SEPARATOR, XAD RESIN, LC CUT #3 IR

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2955-2854	S	aliphatic CH stretch
1745-1730	W	ester or aliphatic ketone
1465, 1381	W	aliphatic CH bend
1262, 1162, 1080	W	aromatic ester or ether, aliphatic ether
801, 719	W	sub. aromatic compds

2. Unassigned weak bands: 1481, 1038, 668 cm^{-1}

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques. Spectrum inculdes peaks of I∿Intensity of blanks. Sample appears to contain only aliphatic esters of aromatic acids, or aliphatic ketones.

TABLE A-11. FROTH FLOTATION SEPARATOR, XAD RESIN, LC CUT #4, IR

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2955-2854	S	aliphatic CH stretch
1756-1715	W	ketone or ester
1462, 1453	W	aliphatic CH bend
1380, 1368	W	gem,-dimethyl bend
746	W	sub benzene

2. Unassigned weak bands: 1271, 1163, 1072

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Spectrum appears to contain predominantly alkylated aromatic hydrocarbons and aliphatic ketones or esters of aromatic acids.

TABLE A-12. FROTH FLOTATION SEPARATOR, XAD RESIN, LC CUT #5, IR

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3350	broad	alcohol or phenol OH
3062	W	aromatic CH stretch
2959, 2932, 2856	S	aliphatic CH stretch
1726	M	aliphatic ketone, or ester
1602	M	aromatic C$\overline{\cdots}$C stretch
1465, 1376	M,W	aliphatic CH bend
1287, 1253	M	ester of aromatic acid, or alcoholic or phenolic C-O
1123, 1075	W	ester of 10 and/or 20 alc.
753, 698	W	mono-sub. benzene

2. Unassigned weak bands: 1513, 1493, 1027 cm^{-1}

3. Other remarks:

Sample contains primarily sat. hydrocarbons, aliphatic esters of aromatic acids, predominantly benzoates, and alcohols or phenols.

TABLE A-13. FROTH FLOTATION SEPARATOR, XAD RESIN
LC CUT #6, IR

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2956, 2927, 2854	S	aliphatic CH stretch
1729	S	ketone or ester
1452	W	aliphatic CH bend
1380, 1371	W	geminal-dimethyl CH bend
758, 743	W	substituted aromatic
1258, 1244	W	ester of aromatic acid, or aromatic and/or aliphatic ethers
1077, 1032	M	

2. Unassigned weak bands: 1601, 1464 cm^{-1}

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample contains predominantly alkylated aromatic esters and/or ethers.

TABLE A-14. FROTH FLOTATION SEPARATOR, XAD RESIN, LC CUT #7, IR

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2962, 2930, 2854	S	aliphatic CH
1744, 1732	S	aliphatic ketone, or ester
1451, 1380	W	aliphatic CH bend
1258, 1076, 1032		acetates of primary or secondary alcohols, or aromatic ethers
758, 743, 723	W	sub. aromatic cmpds

2. Unassigned weak bands: 3367, 3091, 1604, 1553, 1121

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample appears to contain predominantly aliphatic esters (acetates), cyclic saturated ketones, and some aromatic material.

TABLE A-15. ORGANIC EXTRACT SUMMARY, FROTH FLOTATION SEPARATOR, CANISTER RINSE

	Preliminary	Concentrate	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total organics mg/sm^3	29.8	6.1	0.82	0.53	0.53	0.17	0.13	0.86	0.18	3.22
TCO, mg	360		0.0	2.0	0.4	0.0	0.0	1.4	0.0	3.8
GRAV, mg	493	174	23.4	15.1	14.7	4.9	3.7	23.2	5.3	90.3
Category				MATE comparison value, mg/sm^3*						
Aliphatic hydrocarbons			0.82							0.82
Halogenated aliphatics			0.08							0.08
Aromatic hydrocarbons				0.53	0.51	0.17	0.13	0.81	0.18	2.33
Halogenated aromatics			0.05	0.05	0.02					0.12
Heterocyclic N,O,S compounds						0.02	0.01			0.03
Sulfides, disulfides						0.02	0.01			0.03
Nitriles						0.02	0.01			0.03
Ethers						0.02	0.13			0.15
Aldehydes, ketones							0.01	0.81	0.18	1.00
Nitroaromatics							0.01	0.08		0.09
Alcohols							0.13	0.08	0.02	0.23
Amines						0.17	0.13	0.81	0.18	1.29
Phenols, halo and nitrophenols							0.13	0.08	0.02	0.23
Esters, amides							0.13	0.81	0.18	1.12
Mercaptans								0.08	0.02	0.10
Carboxylic acids								0.08	0.02	0.10
Sulfoxides								0.08	0.02	0.10

NOTES: The MATE Comparison Value is based on the GRAV mass in the LC cut divided by the gas sample volume. For compound classes indicated by IR, the MATE comparison value is 100 percent of the GRAV concentration. For compound classes expected [65] but not identified by IR, the MATE Comparison Value is 10 percent of the GRAV concentration.

TABLE A-16. FROTH FLOTATION SEPARATOR, CANISTER RINSE: PRELIMINARY IR

SAMPLE: 1XR-P

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3050	W	aromatic CH stretch
2970, 2925, 2848	W	aliphatic CH stretch
1720, 1712	W	aliphatic ketone and esters
1640, 1595	W	aromatic $C \overset{\cdots}{-} C$
1440, 1420, 1375	M,M,W	aliphatic CH bend
1265	S	ester of α,β-unsat. or aromatic acid or aromatic ester
1140-1125, 1070	W	aromatic and/or aliphatic ethers or aromatic esters
890	W	substituted aromatic cmpds
860-700	W	
700-650	W	

2. Unassigned weak bands: 2550, 2540, 2400, 1070-970 (series of weak bands)

3. Other remarks:

Sample contains predominantly unsat.and/or aromatic ethers and esters of aromatic acids or aroatic ethers. Bands at 1712, 1440, and 1420 cm^{-1} suggest that aliphatic ketones or esters of saturated acids are present: [$-CH_2-(C=O)-$ absorbs at 1420] spectrum dominated by band at 1265 cm^{-1} suggesting sample predominantly aromatic ethers.

TABLE A-17. FROTH FLOTATION SEPARATOR, CANISTER RINSE: CONCENTRATE IR

SAMPLE: 1XR-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3043, 3007	W	aromatic or olefinic CH
2959, 2946, 2856	S	aliphatic CH
1737	M	ester or aliphatic ketone
2061-1936	W	aromatic overtones/combinations
1598	M	aromatic C$\overset{\cdots}{-}$C
1452, 1380	M,W	aliphatic CH bend
1259	M	ester of aromatic or α,β-unsat. acid
1096, 1023	M,W	ester, aliphatic ether
842, 812, 751	W,W,M	sub. aromatic cmpds

2. Unassigned weak bands: 2366, 878, 751 cm^{-1}

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample appears to contain primarily esters of aromatic or α,β-unsat. acids and 1° and/or 2° alcohols. Peak at 1598 cm^{-1} due to org. nitrates or substituted aromatic cmpds. which occasionally show a large, broad unresolved peak in this region.

TABLE A-18. FROTH FLOTATION SEPARATOR, CANISTER RINSE: LC CUT #1 IR

SAMPLE: 1XR-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2931, 2856	S	aliphatic, CH stretch
1465	M	aliphatic, CH bend
1376	W	isolated methyl, CH bend
718	W	$-(CH_2)_4-$ rocking

2. Unassigned weak bands: 1739, 670

3. Other remarks:

Sample predominantly sat. hydrocarbons, containg a trace of ketone.

TABLE A-19. FROTH FLOTATION SEPARATOR, CANISTER RINSE: LC CUT #2 IR

SAMPLE: 1XR-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3048	M	aromatic C-H
2925, 2852	M	aliphatic C-H
1602	M	aromatic
1452	M	aromatic, methyl
842-705	S	aromatic aliphatic

2. Unassigned weak bands: 1925, 1301, 1246, 1185, 1136, 1034

3. Other remarks:

High concentration of aromatic material.

TABLE A-20. FROTH FLOTATION SEPARATOR, CANISTER RINSE: LC CUT #3 IR

SAMPLE: 1XR-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3052	S	aromatic or olefinic CH
2957, 2926, 2857		aliphatic CH
1927, 1000, 1780		aromatic combinations and overtones
1599		aromatic or olefinic C-C
1456, 1440		aliphatic CH
1382		methyl CH
1195-1025		fingerprint region-aromatics
880, 843, 811, 744, 748	S	substituted aromatic cmpds

2. Unassigned weak bands: 1731, 949, 711, and 690 cm^{-1}

3. Other remarks:

Sample contains significant amounts of aromatic hydrocarbons.

TABLE A-21. FROTH FLOTATION SEPARATOR, CANISTER RINSE: LC CUT #4 IR

SAMPLE: 1XR-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3502	S	2° amine
3055	M	aromatic or olefinic CH stretch
2959, 2925, 2856	S	aliphatic CH stretch
1925-1712	W	aromatic combination/overtones
1602	M	aromatic or olefinic $C\overset{\cdots}{-}C$
1459, 1451	S	aliphatic CH bend
1376	W	methyl CH bend
1263-1017	M-W	fingerprint region aromatic
804, 746, 725	M-S	substituted aromatic cmpds.

2. Unassigned weak bands: 2226, 1492, 1326, 867, 842, 700, 616 and 566 cm^{-1}

3. Other remarks:

Probable alkylated aromatic amines.

TABLE A-22. FROTH FLOTATION SEPARATOR, CANISTER RINSE: LC CUT #5 IR

SAMPLE: 1XR-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3357	W (broad)	alcoholic or phenolic OH or amine
3055	W	aromatic CH
2959, 2932, 2856	S	aliphatic CH
2226, 2075	W	conjugated C≡N, or unsymmetric disub. acetylenic -C≡C-
1733	M	ester or aliphatic ketone
1602	M	aromatic $C\overset{\cdots}{-}C$
1458, 1376	M,W	aliphatic CH bend
1260	M	phenolic C-O aromatic ether, ester or aromatic amine
1095, 1027	M	ester, alchohol, phenol, 2° aromatic amine
801, 753	M,W	substituted aromatic CH bend

2. Unassigned weak bands: 1177, 876, 690 cm^{-1}

3. Other remarks:

Shape peak at 1260 possibly due to Ø-NH-R absorption.

Sample predominantly alkylated phenols or secondary aromatic amines, or aromatic esters.

TABLE A-23. FROTH FLOTATION SEPARATOR, CANISTER RINSE:
LC CUT #6 IR

SAMPLE: 1XR-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3062	W	aromatic CH stretch
2959, 2932, 2856	S	aliphatic CH stretch
2062	M	ketene or ketenimine, or keazoketone
1740	M	ketene, ester or aliphatic ketone
1650	M	aliphatic diazoketone
1602	M	aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1452, 1376	M	aliphatic CH
1267-1177	M	aliphatic or aromatic C-O
828, 752	W,M	substituted aromatic

2. Unassigned weak bands: 1109, 1020 and 704 cm^{-1}

3. Other remarks:

Sample predominantly aromatic and saturated and/or unsaturated hydrocarbons but does appear to contain some aliphatic esters and aliphatic diazoketones.

TABLE A-24. FORTH FLOTATION SEPARATOR, CANISTER RINSE: LC CUT #7 IR

SAMPLE: 1XR-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3055	W	aromatic CH stretch
2959, 2932, 2856	S	aliphatic CH stretch
2062	S	ketene or ketenimine (C=C=O) (>C=C=N-)
1746	M	ketene, ester or aliphatic ketone
1465, 1383	M,W	aliphatic CH bend
1074	M	aromatic ester ethyl or n-propyl C-C
821, 753	W	substituted aromatic or ethyl or n-propyl C-C

2. Unassigned weak bands: 1644, 1609, 1348, 1314, 1178, 952 and 691 cm^{-1}

3. Other remarks:

Band at 3261 cm^{-1} believed to be due to presence of H_2O in IR cell.

No strong bands in region 1300-1000 cm^{-1} except at 1074 cm^{-1} suggest that absorption at 1746 cm^{-1} due to ester of saturated acid.

Sample predominantly saturated esters, ketenes, or ketenimines.

TABLE A-25. CYANIDE GAS TRAIN DATA

Run	1	2
Sampling Location	Final Cooler Cooling Tower	Final Cooler Cooling Tower
Volume Metered (scf)	0.732	0.962
Catch (CN^-) (mgms)	1.92	2.16
Concentration ppm	82.4	70.5
μgms/scm	92,618	70,284

TABLE A-26. GAS TRAIN DATA SHEET

Run #1

Plant Name: U.S. Steel

Location: Birmingham, Alabama

Sampling Location: Final cooling tower

Operator: B. Hawks

Date: 13 December 1977

Test Time:

Start: 0915.00

Finish: 0945.00

Meter Volume:

Start: 066.560

Finish: 067.286

Volume Sampled: 0.732 scf

ΔH Setting: 2 scfh

Gas Temperature at Meter Box:

Start: 56

Finish: 56

Ambient Temperature:

Start: 52

Finish: 52

Barometric Pressure: 29.50

Comments:

Gas train bubbling through 0.5M NaOH - 60 ml total volume NaOH

TABLE A-27. GAS TRAIN DATA SHEET

Run #2

Plant Name: U.S. Steel

Location: Birmingham, Alabama

Sampling Location: Final cooling tower

Operator: B. Hawks

Date: 13 December 1977

Test Time:

Start: 1015.00

Finish: 1045.00

Meter Volume:

Start: 067.700

Finish: 068.646

Volume sampled: 0.962 scf

ΔH Setting: 2 scfh

Gas Temperature at Meter Box:

Start: 56°

Finish: 60°

Ambient Temperature:

Start: 52°

Finish: 52°

Barometric Pressure: 29.50

Comments:

Gas train bubbling through 60 ml, 0.5M NaOH

TABLE A-28. ON-SITE GC OF FINAL COOLER COOLING TOWER

Sample Name: Final Cooling Tower

Sample Date: 12/13/77

Analysis Date: 12/13/77

C_1-C_7 HYDROCARBONS

Bulb #1

Range	# Peaks	ppm (V/V)
GC 1	1	2.9
2	0	—
3	0	—
4	0	—
5	0	—
6	0	—
7	0	—

Bulb #2

Range	# Peaks	ppm (V/V)
GC 1	1	2.8
2	0	—
3	0	—
4	0	—
5	0	—
6	0	—
7	0	—

AROMATICS (ppm, V/V)

	On-Site		RTI
	Bulb 1	Bulb 2	SS Can
Benzene	5.3	4.7	4.6
Toluene	—	—	—
Ethyl Benzene	NA	NA	—
m & p Xylene	NA	NA	—
o Xylene	NA	NA	—

SULFURS (ppm, V/V)

	On-Site	
	Bulb 1	Bulb 2
H_2S (COS)	2.3	2.4
SO_2	—	—
CS_2	—	—

NA = No Analysis
— = Compound Not Detected

TABLE A-29. SASS TRAIN DATA SHEET

Plant Name: U.S. Steel

Location: Birmingham, Alabama

Date: 12/13/77

Test Performed By: F. H. Phoenix, E. E. Stevenson

Run Number: 2

Sampling Location: Final Cooler Cooling Tower

Pre Leak Test: 0.00

Post Leak Test: 0.02

Test Time:

Start: 9:00

Finish: 12:45

Meter Volume (c.f.):

Start: 682.58

Finish: 1683.15

Volume of Gas Sampled: 1000.57 c.f.

974.75 scf.

Average Gas Temperature (°F)

Ambient: 58°

Sampling Location: -

XAD-2 Resin: 57°

Meter Box: 79°

Comments:

1. No condensate collected
2. Used 30' Teflon line as probe, ran from top of tower to XAD-2 module
3. Sampling performed in 1 of 2 ~8' diameter outlets - velocity taken from fan data
4. Also ran two gas train runs and took hot well and cold well water samples

TABLE A-30. ORGANIC EXTRACT SUMMARY, FINAL COOLER COOLING TOWER, XAD-2 RESIN

	Preliminary	Concentrate	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total organics mg/sm^3	222	61	0.0 (0.82)	37.0 (38.0)	0.76 (1.41)	1.20 (1.63)	0.98 (1.41)	6.74 (8.04)	0.0 (0.87)	46.7 (52.2)
TCO, mg	6,066	1,410	0.0	1,020	21	33	27	186	0.0	1,287
GRAV, mg	60	282	0.0 (22.5)	0.0 (30.0)	0.0 (18.0)	0.0 (12.0)	0.0 (2.12)	0.0 (36.0)	0.0 (24.0)	0.0 (154)
Category			MATE comparison value, mg/sm^3*							
Aliphatic hydrocarbons			(0.82)	(1.08)						0.0 (1.90)
Halogenated aliphatics			(0.08)							0.0 (0.08)
Aromatic hydrocarbons				(1.08)	(0.65)	(0.43)	(0.43)	(1.30)	(0.87)	0.0 (4.76)
Halogenated aromatics				(0.11)	(0.06)	(0.04)				0.0 (0.21)
Heterocyclic N, O, S compounds						(0.04)	(0.04)			0.0 (0.08)
Sulfides, disulfides						(0.04)	(0.04)			0.0 (0.08)
Nitriles						(0.04)	(0.04)			0.0 (0.08)
Ethers					(0.65)	(0.43)	(0.43)		(0.87)	0.0 (2.38)
Aldehydes, ketones					(0.65)	(0.43)	(0.43)	(1.30)	(0.87)	0.0 (3.68)
Nitroaromatics							(0.04)	(0.13)		0.0 (0.17)
Alcohols							(0.04)	(1.30)	(0.08)	0.0 (1.42)
Amines							(0.04)	(0.13)	(0.08)	0.0 (1.42)
Phenols, halo and nitrophenols								(0.13)	(0.08)	0.0 (0.21)
Esters, amides					(0.65)	(0.43)	(0.43)	(1.30)	(0.87)	0.0 (3.68)
Mercaptans								(0.13)	(0.08)	0.0 (0.21)
Carboxylic acids								(0.13)	(0.08)	0.0 (0.21)
Sulfoxides								(0.13)	(0.08)	0.0 (0.21)

NOTES: The MATE Comparison Value is based on the GRAV mass in the LC cut divided by the gas sample volume. For compound classes indicated by IR, the MATE Comparison Value is 100 percent of the GRAV concentration. For compound classes expected[65] but not identified by IR, the MATE Comparison Value is 10 percent of the GRAV concentration.

Values in parentheses are GRAV mass before subtraction of blank. The presence of GRAV mass in the original sample is shown by the Preliminary and Concentrate samples.

TABLE A-31. FINAL COOLER COOLING TOWER VAPOR, XAD-2 RESIN: PRELIMINARY IR

SAMPLE: 2X-P

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3034	W	aromatic or olefinic CH
2966, 2932, 2875, 2864	S	aliphatic CH stretch
1723	S	ketone or ester
1604, 1491	M, W	aromatic or olefinic $C\overset{\cdots}{-}C$
1456, 1377	M, W	aliphatic CH
1269, 1110, 1076	M, S, M	ester or aromatic acid, or aromatic and/or aliphatic ethers
798, 753, 702	W, W, M	sub. aromatic cmpds-2 and 5 adj. hydrogens

2. Unassigned weak bands: 1025 cm^{-1}

3. Other remarks:

Sample contains predominantly aromatic and aliphatic esters and/or ethers. Bands in aromatic CH out-of-plane region suggest monosubstituted and p-disubstituted benzenes are predominant.

TABLE A-32. FINAL COOLER COOLING TOWER VAPOR, XAD-2 RESIN: CONCENTRATE IR

SAMPLE: 2X-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3094, 3053, 3006	W,M,W	aromatic or olefinic CH stretch
2965, 2934, 2865	W	aliphatic CH stretch
1674-1955	W	aromatic overtones/combinations
1597, 1426	M	condensed aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$, α-sub. naphthalenes, conj. vinyl
781-699	S-M	substituted aromatic cmpds
957	M	vinyl CH out-of-plane bend or aromatic in-plane bend

2. Unassigned weak bands: 1568, 1509, 1456, 1391, 1274, 1245

3. Other remarks:

Sample contains predominantly aromatic hydrocarbons. Bands at 1597, 1426, and 781 cm^{-1} highly suggestive of α-substituted naphthyl derivatives. Some saturated hydrocarbons are present as evidenced by weak bands at 2965-2865 cm^{-1}. Strong band at 950 cm^{-1} characteristic of conjugated vinyl group.

TABLE A-33. FINAL COOLER COOLING TOWER VAPOR, XAD-2 RESIN: LC CUT #1 IR

SAMPLE: 2X-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2961, 2972, 2859	S	aliphatic CH stretch
1460, 1375	M, W	aliphatic CH bend

2. Unassigned weak bands:
3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transfor IR Techniques.

Sample contains only saturated hydrocarbons.

TABLE A-34. FINAL COOLER COOLING TOWER VAPOR, XAD-2 RESIN: LC CUT #2 IR

SAMPLE: 2X-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3062, 3024, 3006	W	aromatic or olefinic CH
2962, 2924, 2871	S	aliphatic CH stretch
1604, 1514, 1494	W	aromatic CH bend
1455, 1375	M,W	aliphatic CH bend
800, 755, 735, 699	W,W,W, M	substituted aromatic cmpds predominantly mono-sub. benzene

2. Unassigned weak bands: 1261, 1089, 1029, 886, 868 cm^{-1}
3. Other remarks:

Sample predominantly saturated hydrocarbons containing some substituted aromatic cmpds.

TABLE A-35. FINAL COOLER COOLING TOWER VAPOR, XAD-2 RESIN: LC CUT #3 IR

SAMPLE: 2X-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3030	W	aromatic or olefinic CH
2965, 2930, 2859	S	aliphatic CH stretch
1738	W	ketone or ester
1456, 1380	M	aliphatic CH bend
1263, 1151, 1028	W	ester of aromatic acid, aromatic ether, aliphatic ether
799, 775, 751, 699	W,W,W,M	substituted aromatic CH bend

2. Unassigned weak bands: 1603, 1492, 893

3. Other remarks:

Sample predominantly saturated and aromatic hydorcarbons, with some aromatic and aliphatic esters and/or aromatic and aliphatic ethers present.

TABLE A-36. FINAL COOLER COOLING TOWER VAPOR, XAD-2 RESIN: LC CUT #4 IR

SAMPLE: 2X-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2929, 2859	S	aliphatic CH stretch
1738	M	ketone or ester
1462, 1380	M	aliphatic CH bend
1268, 1116, 1028	M,W,W	ester of aromatic acid (Ø-CO-O) aliphatic or aromatic ether (C-O-C)
799, 752, 711		substituted aromatic cmpds

2. Unassigned weak bands: 1661, 1603, 1069 cm^{-1}

3. Other remarks:

Sample predominantly aliphatic and aromatic hydrocarbons, containing some esters of aromatic acids, and/or aromatic or aliphatic ethers.

TABLE A-37. FINAL COOLER COOLING TOWER VAPOR, XAD-2 RESIN: LC CUT #5 IR

SAMPLE: 2X-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2930, 2859	S	Aliphatic CH stretch
1732	S	Ester or aliphatic ketone
1603	W	Aromatic or olefinic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1462, 1380	M,W	Aliphatic CH bend
1280, 1128	S,M	Aliphatic ester of aromatic acid, aromatic or aliphatic ether
740, 711	W	Substituted aromatic

2. Unassigned weak bands: 1075 cm^{-1}

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample appears to contain predominantly aliphatic esters of aromatic acids and/or aromatic or aliphatic ethers.

TABLE A-38. FINAL COOLER COOLING TOWER VAPOR, XAD-2 RESIN: LC CUT #6 IR

SAMPLE: 2X-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3063	W	aromatic or olefinic CH
2959, 2930, 2859	S	aliphatic CH stretch
1726	S	ester or aliphatic ketone
1603	M	aromatic or olefinic $C\overset{\cdots}{-}C$
1462, 1380	M,W	aliphatic CH
1274, 1116	M,M	ester of aromatic or α,β-unsaturated acids
752, 711, 693	M-W	subsituted aromatic cmpds

2. Unassigned weak bands: 1497 cm^{-1}

3. Other remarks:

Sample predominantly esters of aromatic or α,β -unsaturated acids and primary alcohols.

TABLE A-39. FINAL COOLER COOLING TOWER VAPOR, XAD-2 RESIN: LC CUT #7 IR

SAMPLE: 2X-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2953, 2930, 2859	S	aliphatic CH stretch
1726	M	ester of aliphatic ketone
1603	M	aromatic of olefinic $C\overset{\cdots}{-}C$
1450, 1374	M	aliphatic CH bend
1274, 1045	M	ester of aromatic or α,β -unsat. acid
1110	S	aliphatic ether
722	W	Sub. aromatic, predominantly 4 adj. H

2. Unassigned weak bands: 3323, 3096, 1668, 1556, 940 cm^{-1}

3. Other remarks:

Sample contains predominantly aliphatic ethers with evidence of esters of aromatic or α,β-unsaturated acids.

TABLE A-40. FINAL COOLER COOLING TOWER VAPOR, CANISTER RINSE: MASS OF SAMPLE AND CONCENTRATE

	Equivalent Total Sample Quantities			
Fraction	TCO, mg	GRAV, mg	Total, mg	Total, mg/m^3
Preliminary	138	16.0	154.0	5.6
Concentrate	0.0	11.0	11.0	0.40
LC1 LC2 LC3 LC4 LC5 LC6 LC7	(TCO + GRAV <15 mg, no LC)			

TABLE A-41. FINAL COOLER COOLING TOWER VAPOR, CANISTER RINSE: PRELIMINARY IR

SAMPLE: 2XR-P

XAD Canister Rinse No. 2
Final Cooler } preliminary sample

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3060	W	aromatic or olefinic CH
2963, 2927, 2862	S	aliphatic CH
1733	S	ester or aliphatic ketone
1603	M	aromatic C--C
1461, 1378	S,M	aliphatic CH
1414	M	α-naphthalene, aliphatic CH
1260	S	aromatic and aliphatic ethers and esters
1088 and 1023	S	aromatic fingerprint region
805 864 and 698	M }	Substituted aromatic CH bend

2. Unassigned weak bands: 2064, 1946 cm^{-1}

3. Other remarks:

Bands at 2363-2340 cm^{-1} are due to presence of CO_2 in cell.

Probable aliphatic esters of aromatic acids, and alkylated aromatic hydrocarbons.

TABLE A-42. FINAL COOLER COOLING TOWER VAPOR, CANISTER RINSE: CONCENTRATE IR

SAMPLE: 2XR-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3070	W	aromatic or olefinic CH
2966-2856	S	aliphatic CH
1740	M	aliphatic ketone or ester
1667	M	aromatic ketone or olefinic C=C
1600	W	aromatic or conj. olefinic C=C
1465	S	aliphatic (methylene) or aromatic C-C
1410	M	α-naphhalene, olefine, or paraffin
1380	M	methyl and α-naphthalene
1264	S	aromatic ethers, or esters
1093-1020	S	aliphatic ethers, aromatic C-C
867-800, 697	S,M	subsittuted aromatic CH bend

2. Unassigned weak bands: 2082, 1947, 666 cm^{-1}

3. Other remarks:

Peaks at 2365-2340 cm^{-1} due to presence of CO_2

Bands at 867, 800, and 697 are suggestive of symmetrically substituted aromatic rings, *e.g.*, 1,3,5-trisubstituted benzene.

Probable aromatic hydrocarbons and alkylated derivatives and unsaturated hydrocarbons.

TABLE A-43. FINAL COOLER COOLING TOWER HOT WELL, pH 2 EXTRACT: MASS OF SAMPLE, CONCENTRATE, AND LC CUTS

	Equivalent Total Sample Quantities		
Fraction	TCO, mg	GRAV, mg	Total, mg
Preliminary	2,160.0	192.0	2,352.0
Concentrate	1,463.0	362.0	1,825.0
LC1	0	25	25
LC2	600	16	616
LC3	0	4	4
LC4	84	12	96
LC5	22	0	22
LC6	574	64	638
LC7	0	12	12
Σ	1,280	133	1,413

TABLE A-44. FINAL COOLER COOLING TOWER HOT WELL, PH2 EXTRACT, PRELIMINARY IR

Insufficient sample before concentration to run IR.

TABLE A-45. FINAL COOLER COOLING TOWER HOT WELL, pH 2 EXTRACT: CONCENTRATE IR

SAMPLE: 9A-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3600, 3470	S	"Free" alcoholic OH, aromatic amines "free" NH
3300-3100	(broad)	NH stretch of H-bonded amine or OH stretch of H-bonded alc.
3030, 3005	S	Aryl or vinyl CH stretch
2920, 2960	S,M	Alkyl CH stretch
1720	S	Aliphatic ketone or ester
1615	S	NH banding of 1° amines
1595, 1500, 1495	S	NH banding of 2° amines + aryl or vinyl $C\overset{\cdots}{-}C$
1455, 1375	S,W	Alkyl, CH bend
1280-1200	M-W	Aromatic CH bends or ester of α,β unsat acids or aromatic acids, aromatic CN stretch, or aryl ether
1150, 1110, 1035	S,W,W	Aliphatic or aromatic ester, aliphatic ether, or amine C-N
835, 730	S,M	Substituted aromatic CH

2. Unassigned weak bands: 1415, 1320, 1175, 930, 880, 690 cm^{-1}

3. Other remarks:

Sample predominantly amines, diphatic ketones or esters of aromatic acids, and some alcoholic compounds.

TABLE A-46. FINAL COOLER COOLING TOWER HOT WELL, pH 2 EXTRACT: LC CUT #1 IR

SAMPLE: 9A-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2964, 2916, 2821	W	Aliphatic CH Stretch
1494	S	Aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1462	S	Aliphatic CH bend, or aromatic
1412, 1377	M	Aliphatic CH band
1333	S	C-N of teriart amine
863, 670	M	Substituted aromatic CH band, alkane, or C-Cl

2. Unassigned weak bands: 1749, 1723, 995 cm^{-1}

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample appears to contain predominantly aliphatic and aromatic tertiary amines.

TABLE A-47. FINAL COOLER COOLING TOWER HOT WELL, pH 2 EXTRACT: LC CUT #2 IR

SAMPLE: 9A-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3055	W	Aromatic C-H, $-CH_2$-halogen
2925, 2856	S	Aliphatic C-H
1725	W	Ketone, ester
1602	W	Aromatic $C\overset{\cdots}{-}C$
1453	M	Aromatic, aliphatic
1376	W	Methyl CH bend
841, 814	M	Aromatic
739	S	Aromatic, C-Cl

2. Unassigned weak bands: 1191, 1034.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

TABLE A-48. FINAL COOLER COOLING TOWER HOT WELL, pH 2 EXTRACT: LC CUT #2 LRMS

SAMPLE: 9A-LC2

1. Categories Present

Intensity	Category
100	PNA's

2. Subcategories, Specific Compounds

Intensity	Subcategory/Compounds
100	Naphthalene, M/e 128
100	Phenanthrene, anthracene, M/e 178
100	Pyrene, M/e 202
100	Chrysene, triphenylene, M/e 252
100	Perylene, benzpyrene, M/e 252
100	Anthanthrene, M/e 276

3. Other

Intensity	Comments
100	M^+/e 152
10	M/e 368. No significant features at M/e greater than 368.
100	Acenaphthylidene?, M/e 152 PNA assignments supported by IR.

TABLE A-49. FINAL COOLER COOLING TOWER HOT WELL, pH 2 EXTRACT: LC CUT #3 IR

SAMPLE: 9A-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3048	M	Aromatic C-H, -CH_2-halogen
2927	S	Aliphatic C-H
2858	M	Aliphatic C-H
1727	W	Ketone, ester
1601	M	Aromatic C$\cdots$C
1450	M	Aliphatic CH bend
1380	W	Methyl CH bend
1264	W	Ester, ether
942	W	Aliphatic, aromatic
882	M	Aliphatic, aromatic
812	M	Aliphatic, Aromatic, C-Cl
745	S	

2. Unassigned weak bands: 1184, 1163, 1033

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Probable PNA hydrocarbon.

TABLE A-50. FINAL COOLER COOLING TOWER HOT WELL, pH 2 EXTRACT: LC CUT #4 IR

SAMPLE: 9A-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3418	S	OH, NH
3062	W	Aromatic C-H
2959, 2933, 2856	W	Aliphatic C-H
1719	W	Ketone, ester
1459	S	Aromatic, aliphatic CH bend
1434	M	Aromatic, methyl, methylene
1095	M	Aromatic
746	S	Multiplet - aromatic, C-Cl

2. Unassigned weak bands:

3. Other remarks:

   2363 and 2336 due to CO_2.

TABLE A-51. FINAL COOLER COOLING TOWER HOT WELL, pH 2 EXTRACT: LC CUT #5 IR

SAMPLE: 9A-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3418	W	OH, NH
2932, 2856	S	Aliphatic C-H
1719	W	Ketone, ester
1458	M	Aromatic, methyl, methylene
746	M	Aromatic, C-Cl
670	S	Aromatic, C-Cl

2. Unassigned weak bands: 1287, 1095, 1013

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

2363 and 2336 due to CO_2. Probable aromatic alcohol or amine.

TABLE A-52. FINAL COOLER COOLING TOWER HOT WELL, pH 2 EXTRACT: LC CUT #6 IR

SAMPLE: 9A-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3363	M	OH
3041	M	Aromatic C-H
2925	S	Aliphatic C-H
2856	M	Aliphatic C-H
1705	S	Ketone, ester
1596, 1506	S	Aromatic $C\overset{\cdots}{-}C$
1459	S	Aliphatic CH bend
1376	M	Methyl CH bend
1287	S	Ether ester of aromatic acid, alcohol, or phenol
753	M	Substituted aromatic CH bend

2. Unassigned weak bands:

3. Other remarks:

   Probable alcohols or alkylated phenols.

TABLE A-53. FINAL COOLER COOLING TOWER HOT WELL, pH 2 EXTRACT: LC CUT #6 LRMS

SAMPLE: 9A-LC6

1. Categories Present

Intensity	Category
NONE	

2. Subcategories, Specific Compounds

Intensity	Subcategory/Compounds
NONE	

3. Other

Intensity	Comments
	No significant ion intensity > ∿ 420 amu
10	Prominent ions (70eV) at M/e 414, 410, 386, 368, 349, 337, 280, 263
100	M/e 195, 149, 123, 109 149 possible phthalate.

TABLE A-54. FINAL COOLER COOLING TOWER HOT WELL, pH 2 EXTRACT: LC CUT #7 IR

SAMPLE: 9A-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3287	W	alcoholic, phenolic, or acidic OH
2927	S	aliphatic C-H
2856	M	aliphatic C-H
1738	S	ketone, ester
1693	M	ketone, acid
1597, 1558	M	aromatic $C\overset{\cdots}{-}C$
1455, 1417	M	aromatic, methyl, methylene

2. Unassigned weak bands: 749

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Probable alkylated phenols, ketones or carboxylic acids.

TABLE A-55. FINAL COOLER COOLING TOWER HOT WELL, pH 12 EXTRACT: MASS OF SAMPLE, CONCENTRATE, AND LC CUTS

	Equivalent Total Sample Quantities		
Fraction	TCO, mg	GRAV, mg	Total, mg
Preliminary	720.0	80.0	800.0
Concentrate	660.0	258.0	918.0
LC1	0.0	0.0	0
LC2	29	0.0	29
LC3	0.0	2.0	2.0
LC4	26	6.0	32.0
LC5	10	0.0	10.0
LC6	417	146	563
LC7	0.0	0.0	0
Σ	482	154	636

TABLE A-56. FINAL COOLER COOLING TOWER HOT WELL, pH 12 EXTRACT: PRELIMINARY IR

SAMPLE: 9B-P

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3300, 3100	M(broad)	alcoholic OH or amine or amide NH
3058	W	aromatic or olefinic CH
2928, 2857	S, M	aliphatic CH
1727	S	ester or aliphatic ketone
1597	S	aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$, amine NH bend
1502	M	aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1455, 1178	S	aliphatic CH bend, ester, aromatic amine C-N
1106, 1059	M	ether, ester, aliphatic amine
746	S(b)	substituted aromatic CH bend and NH bend of 1° amines.

2. Unassigned weak bands: 834, 811 cm^{-1}

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Doubled at 1242 and 1172 cm^{-1} highly suggestive of CN stretching of aromatic amines. Probable alkylated aromatic amines, and esters of aromatic acids.

TABLE A-57. FINAL COOLER COOLING TOWER HOT WELL, pH 12 EXTRACT: CONCENTRATE IR

SAMPLE: 9B-C

1. Major peaks and assignments

$\nu\ (\mathrm{cm}^{-1})$	I	Assignments/Comments
3620	M	alcoholic free OH stretch
3600, 2900	(broad)	alcoholic OH, amide or amine NH
3070, 3006	S	aromatic or olefinic CH stretch
2990, 2959, 2890	S, S	aliphatic CH stretch
1630, 1610	S	1° amine-NH bend, or amide
1590, 1515	M, S	aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1580, 1480	S	aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1450, 1380, 1350	W,M.W	gem-dimethyl CH vibration
1295	M	aromatic amine CH
1260	M(broad)	aliphatic amine CH or alcohol
1190, 1010	M-W	aromatic fingerprint region, ether, alcohol, aliphatic amine or amide.
850, 680	S(broad)	1° and/or 2° amine NH wagging and CH bend of aromatic compounds, including heterocyclic amines
760, 700	M	substituted benzene

2. Unassigned weak bands: 1325, 958, 950, 940 and 895 cm^{-1}

3. Other remarks:

Sample predominantly alcohols, aniline, and alkylated anilines (both N- and ring substituted). Bands at 1380 cm^{-1} and 1350 cm^{-1} suggest that alkylated derivatives are primarily i-pr or t-bu compounds. Also, the series of bands in region of 1630 - 1450 may arise from heterocyclic aromatic amines such as pyridine and quinoline, as well as from the carbon homologs.

TABLE A-58. FINAL COOLER COOLING TOWER HOT WELL, pH 12 EXTRACT: LC CUT #1 IR

SAMPLE: 9B-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2956, 2926, 2859	S	aliphatic CH stretch
1743	W	ester, or aliphatic ketone
1464	M	aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ stretch, or aliphatic CH bend
1452, 1379	W	aliphatic CH bend
723	W	$-(CH_2)_4-$ rocking or substituted aromatic CH bend

2. Unassigned weak bands: 1258, 1021

3. Other remarks:

Sample contains predominantly saturated hydrocarbons and saturated ketones. Possibly small amounts of saturated esters.

TABLE A-59. FINAL COOLER COOLING TOWER HOT WELL, pH 12 EXTRACT: LC CUT #2 IR

SAMPLE: 9B-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2954, 2926, 2858	S	aliphatic CH stretch
1462, 1450	M	aliphatic CH bend
1377	W	methyl CH bend
809	W	substituted aromatic CH bend

2. Unassigned weak bands: 1193, 1143, 1119

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample contains only saturated hydrocarbons with trace amounts of aromatic compounds.

TABLE A-60. FINAL COOLER COOLING TOWER HOT WELL, pH 12 EXTRACT: LC CUT #3 IR

SAMPLE: 9B-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2957, 2928, 2853	S	aliphatic-CH
1733	M	ester or aliphatic ketone
1456, 1375	M	aliphatic CH bend
751	W	$(-CH_2)_4$ - or substituted aromatic

2. Unassigned weak bands: 1687, 1288, 1265

3. Other remarks:

   Probable saturated hydrocarbons.

TABLE A-61. FINAL COOLER COOLING TOWER HOT WELL, pH 12 EXTRACT: LC CUT #3 IR

SAMPLE: 9B-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2929, 2859	S	aliphatic CH stretch
1456	M	aliphatic CH bend
1379	W	methyl CH bend
1262	W	t-butyl
752	W	substituted aromatic CH bend

2. Unassigned weak bands: 1738, 1597, 1380, 1280, 1021

3. Other remarks:

   Probable saturated and alkylated aromatic hydrocarbons.

TABLE A-62. FINAL COOLER COOLING TOWER HOT WELL, pH 12 EXTRACT: LC CUT #4 IR

SAMPLE: 9B-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2956, 2927, 2856	S	aliphatic CH stretch
1735	M	aliphatic ketone or ester
1604, 1496	W	aromatic $C\overset{\cdots}{-}C$ stretch
1455, 1377	M, W	aliphatic CH bend
1276, 1121	W	aromatic ester $\phi-\overset{O}{\overset{\|}{C}}-O$ stretch
745, 698	W	substituted aromatic CH or C-Cl

2. Unassigned weak bands: 1216, 1073 and 1020 cm^{-1}.

3. Other remarks:

Sample appears to be predominantly aliphatic ketones, with some aromatic esters of considerable aliphatic character present.

Shape spike @ 668 cm^{-1} remains unidentified.

TABLE A-63. FINAL COOLER COOLING TOWER HOT WELL, pH 12 EXTRACT: LC CUT #5 IR

SAMPLE: 9B-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2932, 2856	S	aliphatic CH
1733	S	ester or aliphatic ketone
1465	M	aliphatic CH bend
1287, 1274	S	ester of aromatic acid, aromatic ether
1123, 1075	M	ester or ether
746, 695	W	substituted aromatic CH bend, C-Cl

2. Unassigned weak bands: 3244, 1602, 1582, 1383, 952, 876

3. Other remarks:

Probable aliphatic esters of aromatic acids.

TABLE A-64. FINAL COOLER COOLING TOWER HOT WELL, pH 12 EXTRACT: LC CUT #6 IR

SAMPLE: 9B-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3500 - 2500	broad	1° or 2° amines and 1° or 2° amides
3055	S	aromatic CH
2924, 2856	S	aliphatic CH
1595, 1506	S	aromatic C$\overset{\cdots}{-}$C, amide I and II bands
1460, 1376	M	aliphatic CH bend
1246	S	aliphatic or aromatic C-N
807, 699	S	substituted aromatic compounds

2. Unassigned weak bands: 2068, 1924, 1314, 1157, 1040, 944 cm^{-1}

3. Other remarks:

Sample appears to be predominantly aromatic and aliphatic amines or amides.

TABLE A-65. FINAL COOLER COOLING TOWER HOT WELL, pH 12 EXTRACT: LC CUT #7 IR

SAMPLE: 9B-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2953, 2930, 2854	S	alkyl CH stretch
2061	S	isothiocyanate or keterimines (-N=C=S) (C=C=N)
1603	S	unresolved $C\overset{\cdots}{-}C$ stretch of sub. aromatic compound
1462	M	alkyl CH bend
756, 699	M	substituted aromatic CH bend

2. Unassigned weak bands: 1656, 1497, 1280 .

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample contains alkylated aromatic compounds and/or alkyl or aryl isothiocyanates or keterimines.

TABLE A-66. FINAL COOLER COOLING TOWER COLD WELL, pH 2 EXTRACT: MASS OF SAMPLE, CONCENTRATE, AND LC CUTS

	Equivalent Total Sample Quantities		
Fraction	TCO, mg	GRAV, mg	Total, mg
Preliminary	1,360.0	160	1,520.0
Concentrate	862.0	358	1,220.0
LC1	0.0	15	15
LC2	204	0.0	204
LC3	0.0	8	8
LC4	24	8	32
LC5	68	12	80
LC6	562	124	686
LC7	0.0	4	4
Σ	858	171	1,029

TABLE A-67. FINAL COOLER COOLING TOWER COLD WELL, pH 2 EXTRACT: PRELIMINARY IR

SAMPLE: 10A-P

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3500 - 3200	W (broad)	alcoholic or phenolic OH
3056	W	aromatic or olefinic CH
2959, 2918, 2849	M,S,S	aliphatic CH stretch
1712	S	ketone, ester
1689 - 1644		ketone, acid
1603, 1495	M	aromatic $C\overset{\cdots}{-}C$
1461, 1380	M, W	aliphatic CH bend
1243	S (broad)	phenol, alcohol, acid, ester
809, 741, 698	M,S,M	sub. aromatic CH bend

2. Unassigned weak bands: 1724, 1432, 1123, 1009, 837 cm^{-1}

3. Other remarks:

   Probable alkylated phenols and carboxylic acids.

TABLE A-68. FINAL COOLER COOLING TOWER COLD WELL, pH 2 EXTRACT: CONCENTRATE IR

SAMPLE: 10A-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3620, 3500	S	free alcoholic or phenolic OH
3500 - 2900	(2 broad bands)	banded OH-alcohol or phenol
3030	S	aromatic or olefinic CH stretch
2950, 2890	S	aliphatic CH stretch
1712	W	ketone or ester
1630, 1610	S (broad)	substituted aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1520, 1500	S	aromatic or olefinic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1465, 1390, 1365	S,M.M	aliphatic CH bend
1190-1160,1115	S, M	alcoholic or phenolic C-O, or aliphatic ethers
890, 845, 695	W,M,W	substituted aromatic CH

2. Unassigned weak bands: 1422, 1330, 1320, 1290, 1275, 1040, 945 cm^{-1}

3. Other remarks:

Sample predominantly alcohols, and alkylated phenols. Small peak at 1712 cm^{-1} suggests that small quantities of carboxylic acids, ketones, and/or esters might be present.

TABLE A-69. FINAL COOLER COOLING TOWER COLD WELL, pH 2 EXTRACT: LC CUT #1 IR

SAMPLE: 10A-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2949, 2923, 2854	S	alkyl CH stretch
1748, 1711	W	ester and/or ketone
1463, 1379	W	alkyl CH bend

2. Unassigned weak bands: 1154, 1107 cm^{-1}

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample appears to contain only aliphatic hydrocarbons, esters, and ketones.

TABLE A-70. FINAL COOLER COOLING TOWER COLD WELL, pH 2 EXTRACT: LC CUT #2 IR

SAMPLE: 10A-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3045	W	aromatic or olefinic CH
2954,2926,2857	S	aliphatic CH stretch
1726	W	ketone or ester
1459, 1378	M,W	aliphatic CH bend
1261	W	aromatic ester C-CO-O stretch
841 - 699	W	aromatic CH bending (substituted)

2. Unassigned weak bands: 1039, 876 cm^{-1}

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample predominantly saturated and aromatic hydrocarbons, with some aromatic and/or alkyl esters.

TABLE A-71. FINAL COOLER COOLING TOWER COLD WELL, pH 2 EXTRACT: LC CUT #3 IR

SAMPLE: 10A-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2942, 2930, 2859	S	aliphatic CH stretch
1462	M	aliphatic CH bend
840	M	aromatic, unsaturated CH bend
746	S	aromatic CH bend

2. Unassigned weak bands: 881

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Probably alkylated aromatics.

TABLE A-72. FINAL COOLER COOLING TOWER COLD WELL, pH 2 EXTRACT: LC CUT #4 IR

SAMPLE: 10A-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3398	S	phenolic or alcoholic OH
2952, 2932, 2863	S	aliphatic CH stretch
1719	S	ketone/ester
1452	S	aliphatic CH bend
1027	M	ether, aliphatic ester
746, 725	S	$(-CH_2)_4$ or substituted aromatic CH bend

2. Unassigned weak bands:

3. Other remarks:

Probable aliphatic ketones, esters, or ethers and/or alkylated phenols.

TABLE A-73. FINAL COOLER COOLING TOWER COLD WELL, pH 2 EXTRACT: LC CUT #5 IR

SAMPLE: 10A-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3411	S	alcoholic or phenolic OH
3336	M	alcoholic or phenolic OH
2959, 2932, 2856	S	aliphatic CH
1712	M	ketone or ester
1602, 1589	W	aromatic or olefinic $C\overset{\cdot\cdot}{-}C$
1452, 1342	S	aliphatic CH bend
1090, 1013	M	phenolic or alcoholic CO stretch, aliphatic ether or ester
739	S	substituted aromatic CH bend or C-Cl

2. Unassigned weak bands: 1280, 1218, 3055, 698

3. Other remarks:

Probable alkylated phenols and some aliphatic ketones and/or esters.

TABLE A-74. FINAL COOLER COOLING TOWER COLD WELL, pH 2 EXTRACT: LC CUT #6 IR

SAMPLE: 10A-6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3300 - 2500	S(broad)	carboxylic acid OH phenolic OH stretch
3034	S	aromatic CH stretch
2959, 2924, 2863	S	aliphatic CH stretch
1698	S	asym. C=O stretch for saturated and unsaturated/aromatic carboxylic isomer
1595	S	aromatic $\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{C}$
1500 - 1600	M	aromatic $\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{C}$
1458, 1376	M,W	aliphatic CH
1266, 1157, 1026	M	C-O of carboxylic acids and phenols
835, 773, 752, 691	M	aromatic compounds - substituted

2. Unassigned weak bands: 2068, 1869, 931 cm^{-1}.

3. Other remarks:

Sample predominantly aromatic and aliphatic carboxylic acids and/or alkylated phenols.

TABLE A-75. FINAL COOLER COOLING TOWER COLD WELL, pH 2 EXTRACT: LC CUT #7 IR

SAMPLE: 10A-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2962, 2920, 2852	M	alkyl CH stretch
1738	M	ester, or aliphatic ketone
1703	S	ketone or ester
1618, 1439 (?)	M	aromatic or olefinic $\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{C}$
1104, 1042	M	aliphatic ethers, or 2° alcohol

2. Unassigned weak bands: 1676, 863, 834 cm^{-1}

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample appears to contain only residual aliphatic ketones and esters.

TABLE A-76. FINAL COOLER COOLNG TOWER COLD WELL, pH 12 EXTRACT: MASS OF SAMPLE, CONCENTRATE, AND LC CUTS

	Equivalent Total Sample Quantities		
Fraction	TCO, mg	GRAV, mg	Total, mg
Preliminary	480.0	160.0	640.0
Concentrate	356.0	29.0	385.0
LC1	0.0	0.0	0.0
LC2	0.5	0.0	0.5
LC3	0.0	1.0	1.0
LC4	7.5	3.0	10.5
LC5	4.5	1.0	5.5
LC6	239	25	264
LC7	0.0	0.0	0.0
Σ	252	30.0	282

TABLE A-77. FINAL COOLER COOLING TOWER COLD WELL, PH 12 EXTRACT: PRELIMINARY IR

Insufficient sample before concentration to run IR.

TABLE A-78. FINAL COOLER COOLING TOWER COLD WELL, pH 12 EXTRACT: CONCENTRATE IR

SAMPLE: 10B-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3400 - 3000	S(broad)	amine or amide NH stretch
3062	S	aromatic or olefinic CH stretch
2954, 2870	M	aliphatic CH stretch
2151, 2055	W	ketenes (C=C=O) and isothiocyanates
1705, 1664	S	amide I bands (N=C=S) (C=O stretch)
1604, 1515	S	amide II bands (N-H bend) or amine NH bend, or aromatic $C\overset{\cdot\cdot}{-}C$
1500	S	aromatic $C\overset{\cdot\cdot}{-}C$
1445	S	aliphatic CH or saturated 1° amide
1376	M	aliphatic CH bend
1322		aromatic amine C-N
1267 - 1034	W	aromatic fingerprint region and/or amino C-N stretching
900 - 800	M(broad)	amine and/or amide NH bend
746, 691	S,M	monosubstituted benzene

2. Unassigned weak bands: 1548 cm^{-1}.

3. Other remarks:

Sample predominantly aryl and/or alkyl amines and amides; bands at 3062, 1664, 1604, 815, 746 and 691^{+1} strongly suggesting that appreciable amounts of aniline, N-alkylated aniline, and/or amides of benzoic acid are present.

TABLE A-79. FINAL COOLER COOLING TOWER COLD WELL, pH 12 EXTRACT: LC CUT #1 IR

SAMPLE: 10B-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2957, 2928, 2853	S	aliphatic CH stretch
1750	W	ketone or ester
1462, 1375	M, W	aliphatic CH bend

2. Unassigned weak bands: 1467, 722 cm^{-1}

3. Other remarks:

Sample contains predominantly saturated hydrocarbons.

TABLE A-80. FINAL COOLER COOLING TOWER COLD WELL, pH 12 EXTRACT: LC CUT #2 IR

SAMPLE: 10B-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2854, 2956, 2947, 2424	S	aliphatic CH stretch
1457, 1463, 1380	M	aliphatic CH bend
1261, 1161	W	aromatic or aliphatic ether
1015, 1038	W	aromatic or aliphatic ether
810, 804	W	substituted aromatic CH bend or C-Cl

2. Unassigned weak bands: 1600, 1586

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Probable saturated hydrocarbons, with some aromatic or aliphatic ethers.

TABLE A-81. FINAL COOLER COOLING TOWER COLD WELL, pH 12 EXTRACT: LC CUT #3 IR

SAMPLE: 10B-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2929, 2859	S	aliphatic CH stretch
1738	W	ester or aliphatic ketone
1462, 1380	W	aliphatic CH bend
1262	W	alkane, aromatic, aromatic ether, ester of aromatic acid
1028	W	aromatic or aliphetic ether ester of aromatic acid
746, 722	W	$-(CH_2)_4$ - rocking or substituted aromatic CH bend

2. Unassigned weak bands:

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Probable diaphatic esters of aromatic acids, or aliphatic or aromatic ethers.

TABLE A-82. FINAL COOLER COOLING TOWER COLD WELL, pH 12 EXTRACT: LC CUT #4 IR

SAMPLE: 10B-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2929, 2859	S	aliphatic CH stretch
1730	M	ester or aliphatic ketone
1456, 1380	M, W	aliphatic CH bend
1116	W	saturated ester and/or ether
746, 711	W	substituted aromatic CH bend

2. Unassigned weak bands: 1439

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample contains predominantly aliphatic hydrocarbons and/or esters, with some substituted aromatic compounds.

TABLE A-83. FINAL COOLER COOLING TOWER COLD WELL, pH 12 EXTRACT: LC CUT #5 IR

SAMPLE: 10B-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2962, 2923, 2853	W	aliphatic CH stretch
1648	M	term vinyl, NH_2 in plane bending
1508	M	-NH-, aromatic $C\overset{\cdots}{-}C$
1460	M	aliphatic CH, aromatic or olefinic $C\overset{\cdots}{-}C$
680	M	-NH_2- out of plane bending or aromatic CH bend

2. Unassigned weak bands: 1750

3. Other remarks:

Probable saturated and unsaturated hydrocarbons, or alkylated aromatic derivatives.

TABLE A-84. FINAL COOLER COOLING TOWER COLD WELL, pH 12 EXTRACT: LC CUT #6 IR

SAMPLE: 10B-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3671 - 3165	S	alcohol, amine, amide
3062	S	aromatic CH stretch
2925, 2856	S	aliphatic CH stretch
2733, 2603	M	saturated amine
1678	M	amide I band
1596, 1507	S	aromatic C$\overset{\cdots}{-}$C, NH bending of 1° amide or amine
1465, 1376	S, W	aliphatic CH bend
1267 - 1246	S	alcohol, aromatic ether, aromatic amine
1157, 1122, 1040	M	ether, alcohol, phenol, amide NH bend or amine CN
808, 787, 752, 691	S	sub. aromatic CH bend

2. Unassigned weak bands: 1314, 945

3. Other remarks:

   Probable alkylated aromatic amines.

TABLE A-85. FINAL COOLER COOLING TOWER COLD WELL, pH 12 EXTRACT: LC CUT #7 IR

SAMPLE: 10B-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
∿ 3569	S	alcoholic OH, amino NH stretch
3267	S(broad)	alcoholic OH, amine or amide NH
2925, 2856	S	aliphatic CH stretch
2062	M	isothiocyanate
1657	S	conj. olefinic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$, amide I band or amine NH bend
1602	S	aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$, amine or 1° amide NH
1541 - 1507	M	aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$, 2° amide NH
1459, 1376	M	aliphatic CH bend
1287	M	aromatic amine CN stretch, aromatic ether
1123 - 1075	M	alcohol, ether, amine C-N
753 - 698	M	substituted aromatic CH bend

2. Unassigned weak bands: 828 cm^{-1}

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Probable alkylated aromatic amides and amines.

TABLE A-86. SASS TRAIN DATA SHEET

Plant Name: U.S. Steel

Location: Birmingham, Alabama

Date: 12/13/77

Test Performed By: F. J. Phoenix, E. E. Stevenson

Run Number 3

Sampling Location: Tar Storage Tank

Pre Leak Test: 0.02

Post Leak Test: 0.05

Test Time:

Start: 14:55

Finish: 15:44

Meter Volume (c.f.):

Start: 685.67

Finish: 889.97

Volume of Gas Sampled: 202.28 c.f. *

199.06 scf.

Average Gas Temperature (°F)

Ambient: 60°

Sampling Location: 85°

XAD-2 Resin: 80°

Meter Box: 70°

Comments:

1. Naphthalene condensed on XAD-2 Module. We had to take module apart and clean off Naphthalene during run.

* 2.02 c.f. was subtracted from sample volume due to leak check during run.

TABLE A-87. TAR STORAGE TANK

Sample Name: Tar Storage Tank

Sample Date: 12/13/77

Analysis Date: 12/13/77

C_1-C_7 HYDROCARBONS

Bulb #1

Range		# Peaks	ppm (V/V)
GC	1	1	6.6
	2	2	0.9
	3	1	0.1
	4	0	—
	5	0	—
	6	0	—
	7	0	—

Bulb #2

Range		# Peaks	ppm (V/V)
GC	1	1	1.0
	2	2	0.8
	3	1	0.1
	4	0	—
	5	0	—
	6	0	—
	7	0	—

AROMATICS (ppm, V/V)

	On-Site		RTI
	Bulb 1	Bulb 2	SS Can
Benzene	20.6	20.0	20.0
Toluene	5.6	5.5	5.4
Ethyl Benzene	NA	NA	—
m & p Xylene	NA	NA	2.5
o Xylene	NA	NA	1.2

SULFURS (ppm, V/V)

	On-Site	
	Bulb 1	Bulb 2
H_2S (COS)	—	—
SO_2	—	—
CS_2	—	—

NA = No Analysis
— = Compound Not Detected

TABLE A-88. ORGANIC EXTRACT SUMMARY, VAPOR ABOVE TAR STORAGE TANK, XAD-2 RESIN

	Preliminary	Concentrate	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total organics mg/sm³	1,192	1,530	76.3	1,780	148	37.4	24.11	192	10.63	2,270
TCO, mg	6,620	6,090	430	10,040	836	191	96	1,080	0.0	12,700
GRAV, mg	100	2,540	0.0	20	0.0	20	40	0.0	60	140

Category			LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
			MATE comparison value, mg/sm³*							
Aliphatic hydrocarbons			0.0							0.0
Halogenated aliphatics			0.0							0.0
Aromatic hydrocarbons				3.55	0.0	3.55	7.09		10.6	24.8
Halogenated aromatics				0.36	0.0	0.36				0.72
Heterocyclic N, O, S compounds						0.36	0.71			1.07
Sulfides, disulfides						0.36	0.71			1.07
Nitriles						0.36	0.71			1.07
Ethers						3.55	7.09			10.6
Aldehydes, ketones						3.55	7.09		10.6	21.2
Nitroaromatics							0.71			0.71
Alcohols							0.71		1.06	1.77
Amines							0.71		1.06	1.77
Phenols, halo and nitrophenols									1.06	1.06
Esters, amides						3.55	7.09		10.6	21.2
Mercaptans									1.06	1.06
Carboxylic acids									1.06	1.06
Sulfoxides									1.06	1.06

NOTE: The MATE Comparison Value is based on the GRAV mass in the LC cut divided by the gas sample volume. For compound classes indicated by IR, the MATE comparison value is 100 percent of the GRAV concentration. For compound classes expected[65] but not identified by IR, the MATE Comparison Value is 10 percent of the GRAV concentration.

TABLE A-89. VAPOR ABOVE TAR STORAGE TANK, XAD-2 RESIN: PRELIMINARY IR

SAMPLE: 3X-P

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3060, 3031	W	aromatic or olefinic CH
2964, 2930, 2874	S	aliphatic CH stretch
1725	M	ketone or ester
1602, 1495	M	aromatic CH bend
1455, 1376	M,W	aliphatic CH bend
1275, 1106, 1067	M	ester of aromatic acid, aromatic and/or aliphatic ether
802, 751, 701	W,W,M	sub. aromatic CH bend

2. Unassigned weak bands: 1027, 892, 830 cm^{-1}.

3. Other remarks:

Sample predominantly aliphatic and aromatic esters and ethers. IR spectrum suggests that sample is predominantly esters of aromatic acids and alkyl ethers.

TABLE A-90. VAPOR ABOVE TAR STORAGE TANK, XAD-2 RESIN: CONCENTRATE IR

SAMPLE: 3X-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3071, 3054, 3007	W,M,W	aromatic and/or olefinic CH
2967-2863	W	aliphatic CH stretch
1954-1676	W	aromatic overtone region
1595, 1387	M	aromatic or conjugated olefinic $C\overset{\cdots}{-}C$
1213-1011	W	aromatic fingerprint region
958	M	conjugated vinyl CH bend, or aromatic in-plane bend
785-698	S-W	substituted aromatic CH bend

2. Unassigned weak bands: 1566, 1508, 1364, 843 cm^{-1} .

3. Other remarks:

Sample predominantly aromatic and unsaturated hydrocarbons.

TABLE A-91. VAPOR ABOVE TAR STORAGE TANK, XAD-2 RESIN: LC CUT #1 IR

SAMPLE: 3X-LC1-sub H_2O

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2975, 2936, 2859	S	aliphatic CH
1513, 1464	M	aliphatic stretch
1282, 1216, 970	M	aliphatic stretch

2. Unassigned weak bands:

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Probable aliphatic hydrocarbons.

TABLE A-92. VAPOR ABOVE TAR STORAGE TANK, XAD-2 RESIN: LC CUT #2 IR

SAMPLE: 3X-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3060, 3025	W	aromatic CH stretch
2963, 2924, 2857	S	aliphatic CH stretch
1604, 1494	W	aromatic C--C stretch
1455, 1375	M,W	aliphatic CH bend
800, 752	W	sub. aromatic CH bend
752, 699	W,M	sub. aromatic CH bend

2. Unassigned weak bands: 1589, 1535, 1261, 1029, 889.

3. Other remarks:

Sample predominantly saturated hydrocarbons and mono-substituted benzene.

TABLE A-93. VAPOR ABOVE TAR STORAGE TANK, XAD-2 RESIN: LC CUT #3 IR

SAMPLE: 3X-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3025	W	aromatic CH stretch
2961, 2926, 2854	S	aliphatic CH stretch
1741, 1732	W	ester of aromatic acid, Ø-CO-O
1603, 1588, 1494	W	aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ stretch
1462, 1453, 1377	W	aliphatic CH bend
799, 758, 705	W,W,M	sub. aromatic cmpds, primarily monosub. benzene

2. Unassigned weak bands: 1263, 1072, 1031, 893 cm^{-1}.

3. Other remarks:

Sample predominantly saturated hydrocarbons, sat. ketones or ester, containing trace of aromatic cmpds.

TABLE A-94. VAPOR ABOVE TAR STORAGE TANK, XAD-2 RESIN: LC CUT #4 IR

SAMPLE: 3X-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2930, 2859	S	aliphatic CH stretch
1726	M	ester, or aliphatic ketone
1462	M	aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1456, 1380	M,W	aliphatic CH bend
1268, 1110, 1028	M,W,W	ester of aromatic acid, aromatic and/or aliphatic ether
799, 752, 711	W,W,M	substituted aromatic

2. Unassigned weak bands: 1585, 1069 cm^{-1}.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample contains predominantly alkylated esters of aromatic acids, and/or saturated hydrocarbons.

TABLE A-95. VAPOR ABOVE TAR STORAGE TANK, XAD-2 RESIN: LC CUT #5 IR

SAMPLE: 3X-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2932, 2856	S	aliphatic CH stretch
1726	S	ester, or aliphatic ketone
1459, 1376	M,W	aliphatic CH bend
1274, 1116, 1075	S,W	ester of aromatic acid, aromatic or aliphatic ether
801, 746, 712	W	substituted aromatic

2. Unassigned weak bands: 1027 cm^{-1}.

3. Other remarks:

This sample possessed less mas than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample predominantly saturated hydrocarbons and alkyl esters of aromatic acids and/or alkyl and aryl ethers.

TABLE A-96. VAPOR ABOVE TAR STORAGE TANK, XAD-2 RESIN: LC CUT #6 IR

SAMPLE: 3X-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3600-3200	W(broad)	alcoholic or phenolic OH
3065, 3029	W	aromatic or olefinic CH stretch
2959, 2928, 2883	S	aliphatic CH stretch
1726	S	ester or aliphatic ketone
1604, 1514, 1497	M,W,M	aromatic or conj. olefinic C$\overset{\cdots}{-}$C
1464, 1456	S	aliphatic CH bend
1378, 1357	M	gem-dimethyl CH bend
1273, 1113		ester of aromatic acid
1220-1080	M	aromatic fingerprint region
749, 711, 699	W-M	substituted aromatic CH bend

2. Unassigned weak bands: 1681, 1312, 1029, 1022, 824, 800 cm^{-1}.

3. Other remarks:

Sample predominantly alkylated esters of aromatic acids and alcohols.

TABLE A-97. VAPOR ABOVE TAR STORAGE TANK, XAD-2 RESIN: LC CUT #7 IR

SAMPLE: 3X-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3082, 2065, 3030	W	aromatic or olefinic CH
2957, 2927, 2854	S	aliphatic CH stretch
1746	M	ester or aliphatic ketone
1604, 1586, 1497	M,W,S	aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1455, 1357	S,M	aliphatic CH bend
1220, 1148	S,M	aliphatic ester of aromatic acid
752, 732, 699	M,M,S	sub. aromatic, predominantly monosub benzene

2. Unassigned weak bands: 1080, 1029, 988, 934, 886

3. Other remarks:

Sample predominantly ester of aromatic or α,β-unsaturated acid and primary alcohols.

TABLE A-98. ORGANIC EXTRACT SUMMARY, VAPOR ABOVE TAR STORAGE TANK, CANISTER RINSE

	Preliminary	Concentrate	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total organics mg/sm^3	293	132	5.90	70.1	81.6	0.86	0	4.3	0.0	162
TCO, mg	1,545		24.2	364	453	2.42	0.0	24.2	0.0	868
GRAV, mg	109 (spill)	743	9.10	31.5	7.28	2.42	0.0	0.0	0.0	50.3
Category			MATE comparison value, mg/sm^3*							
Aliphatic hydrocarbons			1.6							1.6
Halogenated aliphatics			0.16							0.16
Aromatic hydrocarbons				5.6	1.3	0.43				7.33
Halogenated aromatics				0.56	0.13	0.04				0.73
Heterocyclic N,O,S compounds						0.04				0.04
Sulfides, disulfides						0.04				0.04
Nitriles						0.04				0.04
Ethers			1.6	5.6	1.3	0.43				8.93
Aldehydes, ketones				5.6	1.3	0.43				7.33
Nitroaromatics										0.0
Alcohols				5.6						5.6
Amines										0.0
Phenols, halo and nitrophenols				5.6						5.6
Esters, amides			1.6	5.6	1.3	0.43				8.9
Mercaptans										0.0
Carboxylic acids										0.0
Sulfoxides										0.0

NOTE: The MATE Comparison Value is based on the GRAV mass in the LC cut divided by the gas sample volume. For compound classes indicated by IR, the MATE comparison value is 100 percent of the GRAV concentration. For compound classes expected[65] but not identified by IR, the MATE Comparison Value is 10 percent of the GRAV concentration.

TABLE A-99. VAPOR ABOVE TAR STORAGE TANK: CANISTER RINSE: PRELIMINARY IR

Insufficient sample before concentration to run IR.

TABLE A-100. VAPOR ABOVE TAR STORAGE TANK, CANISTER RINSE: CONCENTRATE IR

SAMPLE: 3XR-C

XAD Canister Rinse No. 3
Tar Storage Rinse

concentrate of no. 9

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3071, 3053, 3035	W,M,W	aromatic or olefinic CH stretch
2980	W	aliphatic CH stretch
1595-1502	W	aromatic C—C stretch
1388	M	α-naphthalenes
1354	W	methyl CH
960	M	H-C=C-H trans or aromatic CH
846	W	aromatic or olefinic CH
780	S	substituted aromatic CH

2. Unassigned weak bands: 1274, 1127, 1007 cm^{-1}.

3. Other remarks:

Inverted peaks at 2365-2340 cm^{-1} are due to presence of CO_2.

This sample was known to contain significant amounts of naphthalene (which crystallized out upon concentration), and the above unassigned weak bands are believed to be due to the presence of these aromatic cmpds, which give rise to several bands in the region 950-1200 cm^{-1}; the fingerprint region for aromatic cmpds.

TABLE A-101. VAPOR ABOVE TAR STORAGE TANK, CANISTER RINSE: LC CUT #1 IR

SAMPLE: 3XR-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2924, 2856	S	aliphatic CH stretch
1733	M	ester or aliphatic ketone
1459	M	aliphatic CH
1376	W	methyl CH
1274	W	conjugated ester or ether C-O or Si-C

2. Unassigned weak bands: 1561, 1123, 1068, 718, 671.

3. Other remarks:

Probable saturated hydrocarbons with trace of aromatic ether or ester of aromatic acid.

TABLE A-102. VAPOR ABOVE TAR STORAGE TANK, CANISTER RINSE: LC CUT #2 IR

SAMPLE: 3XR-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3600-3000	M(broad)	alcoholic or phenolic OH
3048		aromatic CH
2959, 2931, 2856	S	aliphatic CH
1719	S	ketone, ester
1452, 1376	M	aliphatic CH bend
1260	M	ether, ester, alcohol, phenol
1095, 1034	M	ether, alcohol, phenol, ester of aromatic acid
810	M	monosubstituted benzene
739	M	

2. Unassigned weak bands: 1630, 1239, 1164, 864 cm^{-1}.

3. Other remarks:

Probable aliphatic esters of aromatic acids and alcohols.

TABLE A-103. VAPOR ABOVE TAR STORAGE TANK, CANISTER RINSE: LC CUT #3 IR

SAMPLE: 3XR-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3055, 3041	M	aromatic CH stretch
2959, 2932, 2856	S	aliphatic CH stretch
1925	M	aromatic sub.
1732, 1718	M	ketone, ester
1459, 1376	S	aliphatic CH bend
1260, 1089, 1020, 958	M	ester or ether, aromatic CH bend
780, 746, 712	S	substituted aromatic CH bend

2. Unassigned weak bands: 1390, 671, 670, 1616.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Probable alkylated aromatic ethers and alkylated aromatic hydrocarbons.

TABLE A-104. VAPOR ABOVE TAR STORAGE TANK, CANISTER RINSE:
LC CUT #4 IR

SAMPLE: 3XR-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2932, 2856	S	aliphatic CH stretch
1733	S	ester or aliphatic ketone
1459, 1376	M.W	aliphatic CH bend
1287, 1123, 1075	S,M.W	ester of aromatic acid and/ or aryl and alkyl ethers
739, 660	M	monosubstituted benzene

2. Unassigned weak bands:

3. This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Spectrum strongly suggests that sample is predominantly benzoates of 1° and 2° alcohols.

TABLE A-105. VAPOR ABOVE TAR STORAGE TANK, CANISTER RINSE: LC CUT #5 IR

SAMPLE: 3XR-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2961, 2929, 2861	S	aliphatic CH
1733	S	ester or aliphatic ketone
1457	M	aliphatic CH bend
1376	W	methyl CH bend
1276, 1126	M	aliphatic ester of aromatic acid
1075, 744	W,M	substituted aromatic CH or ethyl C-C
744, 701	M	substituted aromatic CH

2. Unassigned weak bands: 1038 cm^{-1}.

3. Other remarks:

Sample predominantly aliphatic esters and/or sat. hydrocarbons but bands at 1075, 1038, 744, and 701 cm^{-1} suggest presence of same aromatic cmpds.

TABLE A-106. VAPOR ABOVE TAR STORAGE TANK, CANISTER RINSE:
LC CUT #6 IR

SAMPLE: 3XR-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3215	W	alcoholic or phenolic OH
3055	W	aromatic CH stretch
2959, 2432, 2856	S	aliphatic CH stretch
1739	S	ester or aliphatic ketone
1602	M	aromatic $C\overset{\cdots}{-}C$
1465, 1383	M	aliphatic CH bend
1267, 1	M	ester of aromatic acid or aliphatic or aromatic ethers
1178, 1143, 1130 1025	W	
746	M	substituted aromatic CH bend

2. Unassigned weak bands: 1026, 965, 835, 761, 698.

3. Other remarks:

   A slight amount of aromatic character.

TABLE A-107. VAPOR ABOVE TAR STORAGE TANK, CANISTER RINSE: LC CUT #7 IR

SAMPLE: 3XR-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3600-3200	W (broad)	alcoholic or phenolic OH
2959, 2932, 2856	S	aliphatic CH stretch
1740	S	ester or aliphatic ketone
1459, 1376	M,W	aliphatic CH bend
1259, 1164, 1075	M	ester of aromatic acid, ether, alcohol, phenol
746	W	substituted aromatic CH bend

2. Unassigned weak bands: 1671, 1602, 1561, 1034, 671 cm^{-1}.

3. Other remarks:

   Probable alcohols and saturated esters.

TABLE A-108. SASS TRAIN DATA SHEET

Plant Name: U.S. Steel

Location: Birmingham, Alabama

Date: 12/14/77

Test Performed By: F. J. Phoenix, E. E. Stevenson

Run Number: 4

Sampling Location: Tar Decanter Tank

Pre Leak Test: 0.00

Post Leak Test: 0.02

Test Time:

Start: 9:00

Finish: 10:40

Meter Volume (c.f.):

Start: 893.59

Finish: 1191.67

Volume of Gas Sampled: 298.08 c.f.

287.41 scf.

Average Gas Temperature (°F)

Ambient: 61°

Sampling Location: 170°

XAD-2 Resin: 100°

Meter Box: 80°

Comments:

1. Used ice bath at sampling location to cool gases before passing through XAD-2 Resin.
2. Ran for ≈ 3-4 minutes when reaction took place in first impinger - Ammonia reacted with hydrogen peroxide - We decided to continue test without first impinger.
3. Sampling performed in one of 4 vents. Tank was leaking vapor in front.

TABLE A-109. TAR DECANTER TANK

Sample Name: Tar Decanter Tank

Sample Date: 12/14/77

Analysis Date: 12/14/77

C_1-C_7 HYDROCARBONS

Bulb #1

Range	# Peaks	ppm (V/V)
GC 1	1	3643
2	1	880
3	4	260
4	1	0.1
5	5	14.1
6	3	31.5
7	1	79

Bulb #2

Range	# Peaks	ppm (V/V)
GC 1	1	3640
2	1	879
3	4	257
4	1	0.1
5	5	14
6	4	144
7	1	97

AROMATIC (ppm,V/V)

	On-Site		RTI
	Bulb 1	Bulb 2	SS Can
Benzene	2190.7	2139.1	2395.6
Toluene	191.5	177.9	214.7
Ethyl Benzene	NA	NA	1.4
m & p Xylene	NA	NA	33.3
o Xylene	NA	NA	7.4

SULFURS (ppm, V/V)

	On-Site	
	Bulb 1	Bulb 2
H_2S (COS)	3792	4571
SO_2	—	—
CS_2	—	—

NA = No Analysis

— = Compound Not Detected

TABLE A-110. ORGANIC EXTRACT SUMMARY, TAR DECANTER VAPOR, XAD-2 RESIN

	Preliminary	Concentrate	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total organics mg/sm^3	6,340	6,820	23.1	1,470	1,370	74	9.2	129	0.0	3,080
TCO, mg	31,520	33,680	0.0	11,025	11,175	600	75	600	0.0	23,475
GRAV, mg	20,080	21,840	188	900	0.0	0.0	0.0	450	0.0	1,540

Category			MATE comparison value, mg/sm^3*							
Aliphatic hydrocarbons			23.1	11.0						133
Halogenated aliphatics			2.3							2.3
Aromatic hydrocarbons				11.0				55.2		165
Halogenated aromatics				11.0						11
Heterocyclic N,O,S compounds										0.0
Sulfides, disulfides										0.0
Nitriles										0.0
Ethers				11.0				55.2		165
Aldehydes, ketones								55.2		55.2
Nitroaromatics										0.0
Alcohols										0.0
Amines										0.0
Phenols, halo and nitrophenols										0.0
Esters, amides			23.1	11.0				55.2		188
Mercaptans										0.0
Carboxylic acids										0.0
Sulfoxides										0.0

NOTE: The MATE Comparison Value is based on the GRAV mass in the LC cut divided by the gas sample volume. For compound classes indicated by IR, the MATE comparison value is 100 percent of the GRAV concentration. For compound classes expected[65] but not identified by IR, the MATE Comparison Value is 10 percent of the GRAV concentration.

TABLE A-111. TAR DECANTER VAPOR, XAD-2 RESIN: PRELIMINARY IR

SAMPLE: 4X-P

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3068, 3056	M	aromatic or olefinic CH
2966, 2931, 2856	W	aliphatic CH
1671, 1958, 1924, 1842, 1787, 1739	W	aromatic combinations/overtones
1595, 1390	M	aromatic or olefinic $C\overset{\cdots}{-}C$, or monosub. naphthalene
1273-1006	W	aromatic fingerprint region
958	M	aromatic or olefinic CH bend
780, 739	S,M	substituted aromatic CH bend

2. Unassigned weak bands: 2294, 1821, 1622, 828, 615

3. Other remarks:

Sample predominantly unsaturated and aromatic hydrocarbons. IR spectrum suggests that aromatic hydrocarbons are predominantly α- and β-substituted naphthalenes.

TABLE A-112. TAR DECANTER VAPOR, XAD-2 RESIN: CONCENTRATE IR

SAMPLE: 4X-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3088, 3071, 3054, 3007	W,M,S,W	aromatic or olefinic CH
2967-2863	W	aliphatic CH
1948-1624	W	aromatic overtones/combinations
1595, 1387	M	condensed aromatic, α-sub. naphthyl, or conj. vinyl $C\overset{\cdots}{-}C$
1271-1010	W	aromatic fingerprint region
958	M	conj. olefinic or aromatic CH
779, 739, 698	S,M,W	substituted aromatic cmpds.

2. Unassigned weak bands: 2290, 1508, 1427, 831, 617.

3. Other remarks:

Sample predominantly naphthalene, substituted aromatic cmpds, and unsaturated hydrocarbons with some aliphatic groups present.

TABLE A-113. TAR DECANTER VAPOR, XAD-2 RESIN: LC CUT #1 IR

SAMPLE: 4X-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2930, 2859	S	aliphatic CH stretch
1739	W	ester or aliphatic ketone
1005	W	aliphatic ester
1457, 1381	M,W	aliphatic CH bend

2. Unassigned weak bands: 1686, 1645, 668 cm^{-1}.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample predominantly saturated hydrocarbons with a trace of aliphatic ketones and/or saturated esters.

TABLE A-114. TAR DECANTER VAPOR, XAD-2 RESIN: LC CUT #2 IR

SAMPLE: 4X-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2930, 2854	S	aliphatic CH stretch
1744	W	ester
1603	W	aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1462, 1380	M,W	aliphatic CH bend
1034	W	aliphatic ester or ether
746	W	substituted aromatic CH bend

2. Unassigned weak bands: 1675, 1151, 816 cm^{-1}.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample predominantly aliphatic hydrocarbons, esters and/or ethers. Bands at 1603 and 746 cm^{-1} suggest aromatic cmpds are predominantly monosubstituted benzene.

TABLE A-115. TAR DECANTER VAPOR, XAD-2 RESIN: LC CUT #3 IR

SAMPLE: 4X-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3072, 3052, 3030	W	aromatic CH stretch
2927, 2860	W	aliphatic CH stretch
1449	W	aliphatic CH bend
1261-1040	W	aromatic fingerprint region
886, 869	W	substituted aromatic CH bend
818	M	
732	S	

2. Unassigned weak bands: 1398, 1301, 954 cm^{-1}.

3. Other remarks:

Sample predominantly aromatic hydrocarbons and alkylated derivatives; *e.g.*, α- and β-substituted naphthalenes.

TABLE A-116. TAR DECANTER VAPOR, XAD-2 RESIN: LC CUT #4 IR

SAMPLE: 4X-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3421, 3395	M,W	1° amine, pyrrole or indole N-H
2955, 2921, 2854	S	aliphatic CH stretch
1723	W	ketone or ester
1462, 1450, 1380	W,M,W	aliphatic CH bend
1263	W	ester of aromatic acid
1098, 1086, 1034	W	aliphatic C-N, aromatic ester, aromatic or aliphatic ethers
805, 749, 725	W,M,S	sub. aromatics CH bend

2. Unassigned weak bands: 1336, 1327, 1239, 1207.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by Fourier Transform IR techniques.

Sample predominantly aromatic and aliphatic hydrocarbons with some aromatic and aliphatic esters and ethers and some 1° amino-cmpds or derivatives of pyrrole and/or indole.

TABLE A-117. TAR DECANTER VAPOR, XAD-2 RESIN: LC CUT #5 IR

SAMPLE: 4X-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2930, 2854	S	aliphatic CH
1728	W	ketone or ester
1462, 1380	W	aliphatic CH
1280	W	acetate, sat. ester

2. Unassigned weak bands: 1034, 740, 670.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analyais. A spectrum of acceptable quality was obtained by Fourier Transform IR techniques.

Sample appears to contain only saturated hydrocarbons and saturated esters.

TABLE A-118. TAR DECANTER VAPOR, XAD-2 RESIN: LC CUT #6 IR

SAMPLE: 4X-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2953, 2930, 2859	S	aliphatic CH stretch
1720	M	ketone or ester
1609	M	aromatic or conj. olefinic $C\overset{\cdots}{-}C$
1462, 1374	M,W	aliphatic CH bend
1245, 1110	W	ester of aromatic acid, or aliphatic and/or aromatic ethers
1028, 1010	W	aromatic fingerprint region
752	W	sub. aromatic CH bend

2. Unassigned weak bands: 1674, 1292 cm^{-1}.

3. Other remarks:

Sample predominantly aliphatic esters of aromatic acids; i.e., benzoates, phthalates, etc.

TABLE A-119. TAR DECANTER VAPOR, XAD-2 RESIN: LC CUT #7 IR

SAMPLE: 4X-7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2929, 2859	S	aliphatic CH stretch
1744	M	ester or aliphatic ketone
1668, 1603, 1556	M	aromatic or olefinic $C \overset{\cdots}{-} C$
1462, 1380	M	aliphatic CH bend
1169, 1110	W,M	aliphatic ester or ether
1075, 1034	W	aromatic fingerprint
722, 828	W	substituted aromatic CH bend

2. Unassigned weak bands: 1415 cm^{-1}.

3. Other remarks:

IR spectrum suggests that sample predominantly aromatic or aliphatic esters of saturated carboxylic acids and aliphatic ethers.

TABLE A-120. ORGANIC EXTRACT SUMMARY, TAR DECANTER VAPOR, CANISTER RINSE

	Preliminary	Concentrate	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total organics mg/sm³	1,220	800	7.68	972	10.7	1.54	4.61	40.7	3.07	1,040
TCO, mg	8,190		0.0	5,520	62.3	0.0	0.0	31.9	0.0	5,900
GRAV, mg	1,760	6,500	62.5	2,390	25.0	12.5	37.5	12.5	25.0	2,565

Category	MATE comparison value, mg/sm³*							
	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Aliphatic hydrocarbons	7.68							7.68
Halogenated aliphatics	0.77							0.77
Aromatic hydrocarbons		294	3.07	1.54	4.61	1.54	3.07	308
Halogenated aromatics		29.4	0.31	0.15				29.9
Heterocyclic N,O,S compounds				0.15	0.46			0.61
Sulfides, disulfides				0.15	0.46			0.61
Nitriles	7.68			0.15	0.46			0.61
Ethers	7.68			1.54	4.6	1.54	3.07	18.4
Aldehydes, ketones	7.68		3.07	1.54	4.6	1.54	3.07	21.5
Nitroaromatics					0.46	0.15		0.61
Alcohols					0.46	0.15	0.31	0.92
Amines			3.07		0.46	0.15	0.31	3.99
Phenols, halo and nitrophenols						0.15	0.31	0.46
Esters, amides	7.68		3.07	1.54	4.6	1.54	3.07	21.5
Mercaptans						0.15	0.31	0.46
Carboxylic acids						0.15	0.31	0.46
Sulfoxides						0.15	0.31	0.46

NOTE: The MATE Comparison Value is based on the GRAV mass in the LC cut divided by the gas sample volume. For compound classes indicated by IR, the MATE comparison value is 100 percent of the GRAV concentration. For compound classes expected[65] but not identified by IR, the MATE Comparison Value is 10 percent of the GRAV concentration.

TABLE A-121. TAR DECANTER VAPOR, CANISTER RINSE: PRELIMINARY IR

SAMPLE: 4XR-P

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3058	M	aromatic CH stretch
2964-2852	W	aliphatic CH stretch
1601	M	conj. DBL-bond, nitroso, aromatic
1495	M	aromatic, nitroso
1447	S	aliphatic CH bend
1265-1023	M	aromatic or vinyl ether, ketal or acetal, C-N stretching, C-O stretching, alkane
952-864	M	epoxy, N-H bending
816	S	aromatic CH bend
781	M	
734	S	

2. Unassigned weak bands: 2339, 1689-2079 cm^{-1}.

3. Other remarks:

2340 & 2370 cm^{-1} due to CO_2.

Probable aromatic hydrocarbons and some aromatic ethers.

TABLE A-122. TAR DECANTER VAPOR, CANISTER RINSE: CONCENTRATE IR

SAMPLE: 4XR-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3090, 3050	S(broad)	aromatic CH stretch
2980-2880	W	aliphatic CH stretch
1950-1650	W	aromatic overtones/ combinations
1595, 1509	S	aromatic $C\overset{\cdots}{-}C$ stretch
1455	W	aliphatic CH bend
1390, 1360	W	gem-dimethyl CH bend
1270-960	S	aromatic fingerprint region
835-700	S(broad)	substituted aromatic CH bend

2. Unassigned weak bands: 1425, 1320, 865 cm^{-1}.

3. Other remarks:

Sample predominantly substituted hydrocarbons. Bands at 1390, 1360, 865 cm^{-1}. Strongly suggest that sample contains significant amounts of α- and β- i-pr and t-bu naphthalenes.

TABLE A-123. TAR DECANTER VAPOR, CANISTER RINSE: LC CUT #1 IR

SAMPLE: 4XR-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2925, 2856	S	aliphatic CH
1733	W	ester, or aliphatic ketone
1465	M	aliphatic CH
1376	W	aliphatic CH
1123 & 1068	W	ester or aliphatic ether
719	W	$-(CH_2)_n^-$ rocking for ≥ 4

2. Unassigned weak bands: 1274 cm^{-1}.

3. Other remarks:

Bands at 1733 cm^{-1} and 1123 and 1068 cm^{-1}. Suggests the presence of trace amounts of esters. Sample predominantly saturated hydrocarbons.

TABLE A-124. TAR DECANTER VAPOR, CANISTER RINSE: LC CUT #2 IR

SAMPLE: 4XR-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3071, 3053	M	aromatic or olefinic -CH
2000-1600	W	aromatic combinations/overtones
1507	M	aromatic $C\overset{\cdots}{-}C$
1392	M	α-naphthalenes $C\overset{\cdots}{-}C$
1200-1000	M	aromatic fingerprint region
957	M	olefinic C-H (trans)
828	M	substituted aromatic hydrocarbons
781	S	
740	S	

2. Unassigned weak bands: 1456, 1445, 1427, 1245, 699, 617 cm^{-1}.

3. Other remarks:

Sample contained virtually no aliphatic hydrocarbons, but appeared to consist almost entirely of aromatic hydrocarbons. Bands at 781 and 740 cm^{-1} highly suggestive of α-naphthalenes, i.e., 3 adjacent hydrogens on a ring or monosubstituted benzene.

TABLE A-125. TAR DECANTER VAPOR, CANISTER RINSE: LC CUT #3 IR

SAMPLE: 4XR-U3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3425	M	aliphatic 2° amine
3055	W	aromatic or olefinic CH stretch
2966, 2925, 2856	M	aliphatic CH stretch
1718	W	ketone or ester
1452	S	aliphatic CH bend
1260-1027	W-M	C-N stretching of aromatic and aliphatic amine
801, 746, 725, 698	M,S,S	substituted aromatic CH bend

2. Unassigned weak bands: 1424, 1335, 993, 931, 890 cm^{-1}.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

The sample seemed to contain predominantly aliphatic 2° amines. The lack of a medium-to-strong band in the region 1650-1580 cm^{-1} arising from 1° amine NH wagging supports the idea that aliphatic 2° amines are predominant. Strong bands in region 890-700 cm^{-1} suggests appreciable amounts of aromatic hydrocarbons.

TABLE A-126. TAR DECANTER VAPOR, CANISTER RINSE: LC CUT #4 IR

SAMPLE: 4XR-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2595, 2932, 2877, 2963	M	aliphatic CH stretch
733	S	ester or aliphatic ketone
1459, 1383	M	aliphatic CH bend
1280, 1274	S	aromatic ether or ester of aromatic acid
1123, 1075	S	aliphatic or aromatic ether or ester of aromatic acid
739	M	substituted aromatic CH bend

2. Unassigned weak bands: 1041, 965, 831, 671.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

3398 due to uneven sample.

671 & 739 may be due to $MeCl_2$.

Probable aliphatic esters of aromatic acids and alkylated aromatic hydrocarbons.

TABLE A-127. TAR DECANTER VAPOR, CANISTER RINSE: LC CUT #5 IR

SAMPLE: 4XR-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3078	W	aromatic or olefinic CH
2963, 2933, 2878, 2866	S	aliphatic CH
1732	S	ester or aliphatic ketone
1599, 1581	W	aromatic or olefinic C—C
1465, 1380	M,W	aliphatic CH bend
1280	S	ester of aromatic acid or aromatic ether
1126, 1071	S	ester of aromatic acid, aliphatic or aromatic ether
744, 701	M.W	substituted aromatic CH bend

2. Unassigned weak bands: 1041, 956, 762 and 653 cm^{-1}.

3. Other remarks:

Sample predominantly aliphatic esters, ethers and/or saturated hydrocarbons, but does contain some aromatic compounds; possibly esters of aromatic acids.

TABLE A-128. TAR DECANTER VAPOR, CANISTER RINSE: LC CUT #6 IR

SAMPLE: 4XR-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3062	W	aromatic or olefinic CH
2966, 2932, 2856	S	aliphatic CH
1740	S	ester, or aliphatic ketone
1609, 1596	M	aromatic or olefinic C=C stretch
1465	M	aliphatic CH bend or aromatic $C\overset{\cdots}{-}C$ stretch
1130, 1074, 1027	W	aromatic $C\overset{\cdots}{-}C$ stretch, aliphatic ether or ester
835	W	$-(CH_2)_4^-$ rocking or substituted aromatic
780, 753	M	substituted aromatic CH bend

2. Unassigned weak bands: 3302, 1643, 1513 cm^{-1}.

3. Other remarks:

- Splitting pattern about 750 cm^{-1} suggests a monosubstituted aromatic compounds are predominant.

- Carbonyl group most likely a keto group due to absence of strong absorption bands @ 1300-1050 cm^{-1} which accompany an ester.

Sample predominantly aliphatic ketones and alkylated aromatic hydrocarbons.

TABLE A-129. TAR DECANTER VAPOR, CANISTER RINSE: LC CUT #7 IR

SAMPLE: 4XR-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3076	W	aromatic CH
2959, 2932, 2856	S	aliphatic CH
1240	S	ester or aliphatic ketone
2082, 1002	W	cyanide
1465, 1376	W	aliphatic CH bend
1247, 1239	S	ester of aromatic acid, or aromatic ether
1212, 1123, 1026	M	ester of aromatic acid, or aromatic or aliphatic ether
746, 615	W	substituted aromatic CH bend

2. Unassigned weak bands: 1582, 1438, 1081, 965, 835, 780, 698.

3. Other remarks:

746, 615, 698 possibly due to $MeCl_2$.

Sample predominantly aliphatic esters of aromatic acids.

TABLE A-130. ORGANIC EXTRACT SUMMARY, TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 2

	Preliminary	Concentrate	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total organics mg/sm^3	207	176	0.61	20.6	19.4	5.65	7.12	96.8	0.0	150
TCO, mg	1,545	923	0.0	108	74	38	42	596	0.0	858
GRAV, mg	138	507	5.0	60	84	8.0	16	192	0.0	365

Category	MATE comparison value, mg/sm^3*							
	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Aliphatic hydrocarbons	0.61							0.61
Halogenated aliphatics	0.06							0.06
Aromatic hydrocarbons		7.37	10.3	0.98	1.96	23.6		44.2
Halogenated aromatics		0.74	1.03	0.10	0.20			2.07
Heterocyclic N,O,S compounds				0.10	0.20			0.30
Sulfides, disulfides				0.10	0.20			0.30
Nitriles				0.10	0.20			0.30
Ethers				0.10	0.20			0.30
Aldehydes, ketones				0.98	1.96	2.36		5.3
Nitroaromatics					0.20	2.36		2.56
Alcohols				0.98	1.96	2.36		5.3
Amines					0.20	2.36		2.56
Phenols, halo and nitrophenols				0.98	1.96	23.6		5.3
Esters, amides				0.98	1.96	2.36		5.3
Mercaptans						2.36		2.36
Carboxylic acids						23.6		23.6
Sulfoxides						2.36		2.36

NOTE: The MATE Comparison Value is based on the GRAV mass in the LC cut divided by the gas sample volume. For compound classes indicated by IR, the MATE comparison value is 100 percent of the GRAV concentration. For compound classes expected[65] but not identified by IR, the MATE Comparison Value is 10 percent of the GRAV concentration.

TABLE A-131. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 2: PRELIMINARY IR

SAMPLE: 11A-P

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3300 - 2500	M	broad O-H stretch of carboxylic acid, alcohol or phenol
3058	M	aromatic CH stretch
2924, 2856	W	aliphatic CH stretch
1691	M	carboxylic acid dimer-asym. -CO-O stretch, aromatic or conj. acid
1594, 1502	M	aromatic or olefinic C$\overset{\cdots}{-}$C
1453, 1380	W	aliphatic CH bend
1246	M	C-O stretch of carboxylic acid or phenol
886, 813, 782 740, 691	W-S-W	substituted aromatic compounds

2. Unassigned weak bands: 1929, 953, 867 cm^{-1}.

3. Other remarks:

1191 - 1039 cm^{-1} aromatic fingerprint region.

Sample predominantly aromatic acids and phenolic derivatives.

TABLE A-132. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 2: CONCENTRATE IR

SAMPLE: 11A-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3590, 3475	S	alcoholic or phenolic free OH
3500 - 2800	(2 broad bands)	alcoholic or phenolic OH H-bonded
3060-3040, 3005	M,S	aromatic or conj. olefinic CH stretch
2975, 2960, 2880	M	aliphatic CH stretch
1620, 1595, 1510, 1500	M,S	aromatic $C\overset{\cdots}{-}C$
1455, 1375	S,W	aliphatic CH bend
1285-1200	M-W	aromatic fingerprint region
1150	S	alcoholic or phenolic C-O
830-750	broad	alcoholic or phenolic OH bend, substituted aromatic CH bend

2. Unassigned weak bands: 1410, 1345, 1315, 1120, 1035, 1000, 930 cm^{-1}.

3. Other remarks:

Sample appears to contain predominantly alcohols and alkylated phenols. Broad, unresolved band at 1595 cm^{-1} strongly suggest that considerable phenolic compounds are present.

TABLE A-133. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 2: LC CUT #1 IR

SAMPLE: 11A-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959	S	aliphatic CH stretch
2925, 2856	S	aliphatic CH stretch
1465	M	aliphatic CH bend

2. Unassigned weak bands: 1376, 1274.

3. Other remarks:

   2340 and 2370 cm^{-1} due to CO_2.

   Only saturated hydrocarbons.

TABLE A-134. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 2: LC CUT #2 IR

SAMPLE: 11A-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3044	W	aromatic CH stretch
2960-2900	W	aliphatic CH stretch
1602	W	aromatic $C\overset{\cdots}{-}C$
1445	W	aliphatic CH bend
815, 732	S	substituted aromatic CH bend

2. Unassigned weak bands: 1623, 1026, 951, 890, 712 cm^{-1}.

3. Other remarks:

   Sample predominantly aromatic.

TABLE A-135. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 2: LC CUT #3 IR

SAMPLE: 11A-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3048	W	aromatic or olefinic CH stretch
2952 - 2850	W	aliphatic CH stretch
1925 - 1602	W	aromatic combination/overtone
1445	M	aromatic or olefinic
1246 - 951	W	fingerprint region-aromatic
814, 732	S	substituted aromatic C-H bend

2. Unassigned weak bands: 1396, 1301, 883, 869, 712 and 698 cm^{-1}.

3. Other remarks:

Sample contained only traces of saturated hydrocarbons - almost entirely aromatic and/or unsaturated hydrocarbons.

TABLE A-136. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 2: LC CUT #4 IR

SAMPLE: 11A-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3423	S	alcoholic or phenolic OH, H-bonded
3047	W	aromatic or olefinic CH stretch
2924, 2854	M	aliphatic CH stretch
1703	W	ketone, ester
1603, 1497	M,W	aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1450	S	aliphatic CH bend
1239, 1886, 1010	M,W,M	alcohol, phenol, ester of aromatic acid
822, 775, 746, 722, 698	M,S,S,S,W	substituted aromatic CH

2. Unassigned weak bands: 1656, 1627, 1339, 1263, 1203, 928 .

3. Other remarks:

Sample contains predominantly phenolic compounds, and some aliphatic esters of aromatic acids.

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

TABLE A-137. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 2: LC CUT #5 IR

SAMPLE: 11A-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3425	S	phenolic or alcoholic OH
3055	W	aromatic or olefinic CH
2959, 2931, 2863	S	aliphatic CH
1726	S	ketone or ester
1452	S	aliphatic CH bend
1280, 1133	S,M	phenol, alcohol, ester or ether
1075, 1006	M	phenol, alcohol, ester or ether
746, 725	S	substituted aromatic CH (suggestive of monosubstituted benzene-phenol?)

2. Unassigned weak bands:

3. Other remarks:

Probable alkylated phenols, diaphatic esters of aromatic acids, ethers, alcohols.

TABLE A-138. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 2: LC CUT #6 IR

SAMPLE: 11A-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3300-2500	S	carboxylic acid or phenolic derivatives
2959, 2931, 2863	S	aliphatic CH stretch
1596, 1506	S	$C\overset{\cdots}{-}C$ ring stretches
1465, 1376	S,M	aliphatic CH bend
1376	M	phenolic OH bend
1246	S	phenolic C-O stretch
1000-1200	W-M	aromatic fingerprint region
691-807	M-S	substituted aromatic CH

2. Unassigned weak bands: 1924, 1623, 1314, 951, 931, and 623 cm^{-1}.

3. Other remarks:
Probable alkylated phenols.

TABLE A-139. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 2: LC CUT #7 IR

SAMPLE: 11A-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
1956, 2929, 2856	S	aliphatic CH stretch
2064	M	isothiocyanate
1731, 1711	S	ketone, ester
1597, 1484	S, M	aromatic or conj. olefinic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1465	M	aliphatic CH bend
1278	S	ester, ether
1125, 1072	W	ester, ether
746	M	alkene, substituted aromatic CH bend

2. Unassigned weak bands: 1551, 1451.

3. Other remarks:

This sample possessed less mass than that required by Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Probable aliphatic esters of aromatic acids.

TABLE A-140. ORGANIC EXTRACT SUMMARY, TAR DECANTER VAPOR, CONDENSATE EXTRACT, pH 12

	Preliminary	Concentrate	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total organics mg/sm^3	59	45	0.46	0.80	0.61	0.43	2.27	26.8	0.12	31.5
TCO, mg	345	338	0.0	6.5	3.0	3.5	15.5	208	0.0	236
GRAV, mg	138	26	3.75	0.0	2.0	0.0	3.0	10.0	1.0	16.8

Category			MATE comparison value, mg/sm^3*							
Aliphatic hydrocarbons			0.46							0.46
Halogenated aliphatics			0.05							0.05
Aromatic hydrocarbons					0.24		0.37	1.23	0.12	1.96
Halogenated aromatics					0.02					0.02
Heterocyclic N,O,S compounds							0.04			0.04
Sulfides, disulfides							0.04			0.04
Nitriles							0.04			0.04
Ethers					0.24		0.04	1.23	0.12	1.63
Aldehydes, ketones					0.24		0.37	0.12	0.12	0.85
Nitroaromatics							0.04	0.12		0.16
Alcohols							0.04	0.12	0.01	0.17
Amines							0.37	1.23	0.01	1.61
Phenols, halo and nitrophenols								0.12	0.01	0.13
Esters, amides					0.24		0.37	1.23	0.12	1.96
Mercaptans								0.12	0.01	0.13
Carboxylic acids								0.12	0.01	0.13
Sulfoxides								0.12	0.01	0.13

NOTE: The MATE Comparison Value is based on the GRAV mass in the LC cut divided by the gas sample volume. For compound classes indicated by IR, the MATE comparison value is 100 percent of the GRAV concentration. For compound classes expected[65] but not identified by IR, the MATE Comparison Value is 10 percent of the GRAV concentration.

TABLE A-141. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 12: PRELIMINARY IR

SAMPLE: 11B-P

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3500 - 3200	W(broad)	amine or amide NH, H-bonded
2954, 2930, 2859	S	aliphatic CH stretch
1743, 1732	M	ester, or possibly aliphatic ketone
1701	W	amide I band of 1° amides, ketone, ester
1462, 1380	M,W	aliphatic CH bend
1262 - 1074	W	amino C-N stretch, esters of aromatic acids, aromatic and/or aliphatic ethers
799, 740	W	amine or amide NH bend, sub. aromatic NH bend

2. Unassigned weak bands:

3. Other remarks:

Sample predominantly aliphatic ketones, and aryl alkyl amines and/or amides. May contain some esters of aromatic acids.

TABLE A-142. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 12: CONCENTRATE IR

SAMPLE: 11B-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3545, 3585	S,W	alcoholic OH stretch
3500-3100	S→M (broad)	amines or amides NH stretch
3050-3030, 3006	S	aromatic CH stretch
2980, 2920, 2865	M,M,W	aliphatic CH stretch
2064	M	isothiocyanate (-N=C=S)
1720	M	aliphatic ketones or esters
1660, 1620, 1590, 1580	S	1° amines, amide I ($>$C=O) and amide II (NH bend) bands, or aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1455, 1375	S,W	aliphatic CH bend
1410	M	1° amide C-N stretch
1265, 1255, 1155-1090	M,M,S→M	esters of aromatic acids, C-N stretch of 1°, 2°, and/or 3° amines and 2° amides or alcoholic C-O
830-730	M	amines and 1° amide NH wag or substituted aromatic CH bend

2. Unassigned weak bands: 2560, 2400, 1500, 1480, 1010, 840 cm^{-1}.

3. Other remarks:

Sample appears to contain predominantly aryl and alkyl amines or amides. The broad unresolved peak about 1600 cm^{-1} is typical of monosubstituted benzene, suggesting the presence of aniline and N-alkylated derivatives.

TABLE A-143. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 12: LC CUT #1 IR

SAMPLE: 11B-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959	S	aliphatic CH stretch
2925, 2856	S	aliphatic CH stretch
1465	M	aliphatic CH bend

2. Unassigned weak bands: 1739, 1376, 1287.

3. Other remarks:

   2340 and 2370 cm^{-1} due to CO_2.

   Only saturated hydrocarbons present.

TABLE A-144. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 12: LC CUT #2 IR

SAMPLE: 11B-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3053	W	aromatic or olefinic CH stretch
2951, 2931, 2846	M,S,M	aliphatic CH stretch
1570, 1472	W,M	aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1450	M	aliphatic CH bend
872	W	isolated aromatic CH bend
810, 739, 692	M,S,S	substituted aromatic CH bend

2. Unassigned weak bands: 1014 cm^{-1}.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample contained saturated and unsaturated or aromatic hydrocarbons.

TABLE A-145. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 12: LC CUT #3 IR

SAMPLE: 11B-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3056, 3044, 3017	W	aromatic or olefinic CH stretch
2950, 2923, 2855	S	aliphatic CH stretch
1730	M	aliphatic ketone or ester
1600, 1583, 1492, 1477	W,W,W,M	aromatic C$\overset{\cdots}{-}$C stretch
1462, 1459, 1442	M	aliphatic CH bend
1374, 1365	W	methyl CH bend, possibly gem-dimethyl
1263, 1092, 1064, 1025	M-S	ester of aromatic acid or aromatic or aliphatic ether
822, 813, 799, 778, 737	M,S,M,S	substituted aromatic isolated H substituted aromatic CH bend

2. Unassigned weak bands: 1201, 1177, 699 cm^{-1}.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by Fourier Transform IR techniques.

Sample appears to contain predominantly aromatic compounds and ester of aromatic acids or aryl ethers.

TABLE A-146. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 12: LC CUT #4 IR

SAMPLE: 11B-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3411	S	2°amine or amide NH stretch
3062	W	aromatic CH stretch
2959, 2931, 2856	S	aliphatic CH stretch
1718	M	ketone, formate or conjugated ester or amide
1459	M	aliphatic CH or amide C-N
1280, 1239	M	amide or aryl alkyl ether
1095, 1013	M	ester, ether
739	S	substituted benzene
691	M	substituted benzene

2. Unassigned weak bands: 1342, 1123, 1075 and 808 cm^{-1}

3. Other remarks:

IR spectrum suggests sample contains appreciable amounts of aromatic and aliphatic 2° amines. Lack of strong absorption at 1718 cm^{-1} suggests that absorption at 3411 cm^{-1} due to 2° amine not amide.

TABLE A-147. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 12:
LC CUT #5 IR

SAMPLE: 11B-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3391	M	2° amine or 2° amide
3055	W	aromatic or olefinic CH
2959, 2911, 2863	S	aliphatic CH
1726	S	ketone or ester
1602, 1581	W	aromatic C$\overset{\cdots}{-}$C
1465, 1388	M,W	aliphatic CH, methyl CH bend
1280, 1123	S,M	aliphatic ester of aromatic acid
1075, 952	M,W	aromatic fingerprint region
734, 691	S,W	substituted benzene, probably ortho-disubstituted

2. Unassigned weak bands: 1581 (probably >N-H bending), 1410, 1239, 952, and 780 cm^{-1}.

3. Other remarks:

Carboryl absorption too high for amide, and lack of doublet in region 3400 - 3100 cm^{-1} leads to conclusion that compounds are secondary amino derivatives. Sample contains aryl and alkyl 2° amines and aryl and/or alkyl esters.

TABLE A-148. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 12: LC CUT #6 IR

SAMPLE: 11B-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3329	M (broad)	alcoholic OH or amide or amine NH
3150, 3068	S	aromatic or olefinic CH stretch
2954, 2931, 2863	S	aliphatic CH stretch
2068	W	isothiocyanate or ketenimine
1725	M	ester and/or aliphatic ketone
1610, 1595, 1506	S	aromatic $C\overset{\cdots}{-}C$ and/or amine or amide NH bend
1459, 1390	S,M	aliphatic CH bend
1287-1246	S	ester of aromatic acid, aryl ether of C-N stretch of aryl or alkyl amines
944, 849, 807-691	W,W,M	sharp bands in aromatic fingerprint region, substituted aromatic CH bend

2. Unassigned weak bands: 2733, 2698, 2575, 1321 .

3. Other remarks:

Sample predominantly alkylated derivatives of aniline or polynuclear aromatic amine, and saturated ketones. The lack of a broad band in region 1250-100 cm^{-1} corresponding to an ethercal or alcoholic C-O stretch suggests that the sharp, strong band in this region is likely due to C-N stretch of amines.

TABLE A-149. TAR DECANTER VAPOR, CONDENSATE EXTRACT pH 12: LC CUT #7 IR

SAMPLE: 11B-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2954, 2931, 2856	S	Aliphatic CH stretch
2061	M	Isothiocyanate or ketenimine
1732	S	Ester or aliphatic ketone
1465	M	Aliphatic CH bend
1240	S	Ester of aromatic acid, aromatic ether
1122, 1074	W	Ether, ester of aromatic acid
739	M	Aromatic

2. Unassigned weak bands: 1664, 1602, 1581, 1383, 759, 691

3. Other remarks:

   Probable aliphatic esters of aromatic acids.

TABLE A-150. LIGHT OIL STORAGE TANK

Sample Name: Light Oil Storage Tank

Sample Date: 12/14/77

Analysis Date: 12/14/77

C_1-C_7 HYDROCARBONS

Bulb #1

Range	# Peaks	ppm (V/V)
GC 1	1	20
2	2	35
3	4	25
4	1	1
5	6	15
6	6	25
7	0	—

Bulb #2

Range	# Peaks	ppm (V/V)
GC 1	1	20
2	2	34
3	4	25
4	1	1
5	6	17
6	6	17
7	1	0.1

AROMATIC (ppm, V/V)

	On-Site		RTI
	Bulb 1	Bulb 2	SS Can
Benzene	306.1	296.3	358.3
Toluene	NA	8.5	10.6
Ethyl Benzene	NA	NA	—
m & p Xylene	NA	NA	—
o Xylene	NA	NA	—

SULFURS (ppm, V/V)

	On-Site	
	Bulb 1	Bulb 2
H_2S (COS)	22	20
SO_2	—	—
CS_2	5-10 ppm (estimate)	

NA = No Analysis
— = Compound Not Detected

TABLE A-151. SASS TRAIN DATA SHEET

Plant Name: U.S. Steel

Location: Birmingham, Alabama

Date: 12/15/77

Test Performed By: F. H. Phoenix, E. E. Stevenson, T. Allen

Run Number: 5

Sampling Location: Chemical Oil Storage Tank

Pre Leak Test: 0.00

Post Leak Test: 0.08

Test Time:

Start: 8:41

Finish: 11:50

Meter Volume (c.f.):

Start: 361.52

Finish: 870.40

Volume of Gas Sampled: 505.48 c.f.*

503.86 scf.

Average Gas Temperature (°F)

Ambient: 50°

Sampling Location: 110°

XAD-2 Resin: 80°

Meter Box: 65°

Comments:

1. Naphthalene was condensing on inside of XAD-2 Module and probe.
* 3.40 cf subtracted due to leak test.

TABLE A-152. CHEMICAL OIL STORAGE TANK

Sample Name: Chemical Storage Tank

Sample Date: 12/15/77

Analysis Date: 12/15/77

C_1-C_7 HYDROCARBONS

Bulb #1

Range	# Peaks	ppm (V/V)
GC 1	1	2.8
2	0	—
3	0	—
4	0	—
5	0	—
6	0	—
7	0	—

Bulb #2

Range	# Peaks	ppm (V/V)
GC 1	1	2.8
2	0	—
3	0	—
4	0	—
5	0	—
6	0	—
7	0	—

AROMATICS (ppm, V/V)

	On-Site		RTI
	Bulb 1	Bulb 2	SS Can
Benzene	97.4	104.9	99.5
Toluene	68.5	69.0	70.5
Ethyl Benzene	NA	NA	5.3
m & p Xylene	NA	NA	40.0
o Xylene	NA	NA	10.8

SULFURS (ppm, V/V)

	On-Site	
	Bulb 1	Bulb 2
H_2S (COS)	—	—
SO_2	—	—
CS_2	—	—

NA = No Analysis
— = Compound Not Detected

TABLE A-153. ORGANIC EXTRACT SUMMARY, VAPOR ABOVE CHEMICAL OIL TANK, XAD-2 RESIN

	Preliminary	Concentrate	LC1	LC2	LC3	LC4	LC5	LC6	LC7	
Total organics mg/sm³	2,110	2,420	10.5 (36.8)	522 (543)	620 (641)	0.0 (21.0)	7.01 (21.0)	210 (238)	0.0 (21.0)	1,370 (1,520)
TCO, mg	26,730	28,800	150	7,450	8,850	0.0	100	3,000	0.0	19,550
GRAV, mg	3,360	5,730	0.0 (375)	0.0 (300)	0.0 (300)	0.0 (300)	0.0 (200)	0.0 (200)	0.0 (300)	0.0 (2,175)

Category			MATE comparison value, mg/sm³*							
Aliphatic hydrocarbons			(26.3)							0.0 (26.3)
Halogenated aliphatics			(2.63)							0.0 (2.63)
Aromatic hydrocarbons				(21.0)	(21.0)	(21.0)	(14.0)	(28.0)	(21.0)	0.0 (126)
Halogenated aromatics				(2.1)	(2.10)	(2.10)				0.0 (6.3)
Heterocyclic N, O, S compounds						(2.10)	(1.4)			0.0 (3.5)
Sulfides, disulfides						(2.10)	(1.4)			0.0 (3.5)
Nitriles						(2.10)	(1.4)			0.0 (3.5)
Ethers				(21.0)	(21.0)	(21.0)	(14.0)	(28.0)	(21.0)	0.0 (126)
Aldehydes, ketones					(21.0)	(21.0)	(14.0)	(28.0)	(21.0)	0.0 (105)
Nitroaromatics							(1.4)	(2.8)		0.0 (4.2)
Alcohols							(1.4)	(2.8)	(2.10)	0.0 (6.3)
Amines							(1.4)	(2.8)	(2.10)	0.0 (6.3)
Phenols, halo and nitrophenols								(2.8)	(2.10)	0.0 (4.9)
Esters, amides					(21.0)	(21.0)	(14.0)	(28.0)	(21.0)	0.0 (105)
Mercaptans								(2.8)	(2.10)	0.0 (4.9)
Carboxylic acids								(2.8)	(2.10)	0.0 (4.9)
Sulfoxides								(2.8)	(2.10)	0.0 (4.9)

NOTE: Values in parentheses are GRAV mass before subtraction of blank. The presence of GRAV mass in the original sample is shown by the Preliminary and Concentrate samples. The MATE Comparison Value is based on the GRAV mass in the LC cut divided by the gas sample volume. For compound classes indicated by IR, the MATE comparison value is 100 percent of the GRAV concentration. For compound classes expected[65] but not identified by IR, the MATE Comparison Value is 10 percent of the GRAV concentration.

TABLE A-154. VAPOR ABOVE CHEMICAL OIL TANK, XAD-2 RESIN: PRELIMINARY IR

SAMPLE: 5X-P

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3069, 3055, 3007	W,M,W	Aromatic CH stretch
2959, 2932, 2856	W	Aliphatic CH stretch
1950, 1924, 1842, 1732	W	Aromatic combinations/overtones
1596, 1506	M	Aromatic C$\overset{\cdots}{-}$C
1390, 1363	M	Highly sub. aromatic or gemdimethyl CH bend
1274, 1173, 1123	W	Aromatic or aliphatic ethers
958	M	
841, 780, 648	W,S,W	Substituted aromatic CH Bend

2. Unassigned weak bands: 1671, 1568, 1246, 1006, 616
3. Other remarks:

Sample appears to contain predominant aromatic hydrocarbons and methylated and/or other alkylated derivatives.

TABLE A-155. VAPOR ABOVE CHEMICAL OIL TANK, XAD-2 RESIN: CONCENTRATE IR

SAMPLE: 5X-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3068, 3051, 3004	W,M,W	Aromatic or olefinic CH
2952-2850	W	Aliphatic CH stretch
1957-1671	W	Aromatic overtones/combinations
1596, 1508	M,W	Aromatic $C\overset{\cdots}{-}C$
1392	M	Highly substituted aromatics
961, 780, 746	M,S,M,M	Substituted aromatic cmpds

2. Unassigned weak bands: 2298, 1270, 1124, 1008, 845, 816 cm^{-1}.

3. Other remarks:

Sample comprised almost entirely of aromatic hydrocarbons with very few saturated or oxygen-containing cmpds present.

TABLE A-156. VAPOR ABOVE CHEMICAL OIL TANK, XAD-2 RESIN: LC CUT #1 IR

SAMPLE: 5X-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2960, 2926, 2858	S	Aliphatic C-H stretch
1462	M	Aliphatic CH Bend
1377	W	Isolated methyl CH bend

2. Unassigned weak bands: 1746, 1604 .

3. Other remarks:

Sample contains predominantly saturated hydrocarbons.

TABLE A-157. VAPOR ABOVE CHEMICAL OIL TANK, XAD-2 RESIN: LC CUT #2 IR

SAMPLE: 5X-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2926, 2856	M,S,M,	Aliphatic CH stretch
1462, 1452	W	Aliphatic CH bend
1380	W	Methyl CH bend
1262	S	Aromatic ether
1098, 1040	S	Aromatic and/or aliphatic ether
802	S	Substituted aromatic CH bend

2. Unassigned weak bands: 863, 750, 701 cm^{-1}.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR Techniques.

Sample predominantly aliphatic and aromatic ethers. Absorption bands in CH out-of-plane bending region for aromatics suggests that para-substituted benzene is predominant but some monosub. benzene is present.

TABLE A-158. VAPOR ABOVE CHEMICAL OIL TANK, XAD-2 RESIN: LC CUT #3 IR

SAMPLE: 5X-LC3

1. Major peaks and assignments

$\nu (cm^{-1})$	I	Assignments/Comments
2965, 2930, 2859	S	Aliphatic CH stretch
1738	W	Ester or aliphatic ketone
1462, 1380	M,W	Aliphatic CH bend
1263	S	Aromatic ether or ester of aromatic acid
1098, 1039	S	Aromatic and/or aliphatic ethers or alkanes
869, 805, 699	W,S,W	Substituted aromatic

2. Unassigned weak bands: 1656, 670 cm^{-1}.

3. Other remarks:

Sample seems to consist primarily of vinyl or aromatic ethers, and a small amount of aromatic or aliphatic esters.

TABLE A-159. VAPOR ABOVE CHEMICAL OIL TANK, XAD-2 RESIN: LC CUT #4 IR

SAMPLE: 5X-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2960, 2920, 2850	S	Aliphatic CH Stretch
1706	W	Ketone or ester
1593	W	Aromatic $C\overset{\cdots}{-}C$
1460, 1375	W	Aliphatic CH bend
1020	W	Aliphatic ester or ether
726	W	Substituted aromatic CH bend

2. Unassigned weak bands:

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample appears to contain predominantly saturated hydrocarbons and a trace amount of aromatic compounds.

TABLE A-160. VAPOR ABOVE CHEMICAL OIL TANK, XAD-2 RESIN: LC CUT #5 IR

SAMPLE: 5X-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2924, 2859	S	Aliphatic CH stretch
1726	M	Ketone or ester
1468, 1450	M, W	Aliphatic CH bend
1380	W	Isolated methyl CH bend
1286, 1130	M, W	Aliphatic or aromatic ester or ether
740	W	Substituted aromatic CH bend

2. Unassigned weak bands: 1661, 1632, 1603, 1074 cm^{-1}.

3. Other remarks:

Sample predominantly saturated hydrocarbons and aliphatic esters. Bands in region 1660-1600 and at 1074 and 740 cm^{-1} suggest presence of aromatic cmpds, possibly alkylated derivatives or aromatic esters.

TABLE A-161. VAPOR ABOVE CHEMICAL OIL TANK, XAD-2 RESIN: LC CUT #6 IR

SAMPLE: 5X-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3063	W	Aromatic or olefinic CH
2956, 2927, 2856	S	Aliphatic CH stretch
1727	S	Ketone or ester
1603, 1460	M	Aromatic C$\overset{\cdots}{-}$C
1454, 1380	M,W	Aliphatic CH bend
1280, 1125	M,W	Ester of aromatic acid or aromatic and/or aliphatic ether
748, 694	M,W	Substituted aromatic CH bend

2. Unassigned weak bands: 1075, 1040, 618 cm^{-1}.
3. Other remarks:

   Sample predominantly aromatic esters of 1° alcohols (i.e., benzoates, etc.)

TABLE A-162. VAPOR ABOVE CHEMICAL OIL TANK, XAD-2 RESIN: LC CUT #7 IR

SAMPLE: 5X-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2964, 2962, 2859	S	Aliphatic CH stretch
1738	M	Ester or aliphatic ketone
1562	M	Aromatic $C\overset{\cdots}{-}C$ stretch
1456	M	Aliphatic CH bend
1286, 1268, 1122	W	Esters of aromatic acids or aromatic or aliphatic ethers
740	W	Substituted aromatic CH bend

2. Unassigned weak bands: 1074, 669 cm^{-1}.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample predominantly saturated ethers or saturated ethers and/or esters of aromatic acids.

TABLE A-163. ORGANIC EXTRACT SUMMARY, VAPOR ABOVE CHEMICAL OIL TANK, CANISTER RINSE

	Preliminary	Concentrate	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total organics mg/sm^3	802	1,550	27	1,584	298	51.4	0.0	72.2	0.0	2,280
TCO, mg	2,480		3,740	16,000	4,260	0.0	0.0	1,030	0.0	25,030
GRAV, mg	8,960	22,120	122	6,610	0.0	734	0.0	0.0	0.0	7,470

Category			MATE comparison value, mg/sm^3*							
Aliphatic hydrocarbons			8.54							8.54
Halogenated aliphatics			0.85							0.85
Aromatic hydrocarbons				463		51.4				514
Halogenated aromatics				46.3		5.14				51.4
Heterocyclic N, O, S compounds						5.14				5.14
Sulfides, disulfides						5.14				5.14
Nitriles						5.14				5.14
Ethers			8.54			51.4				59.9
Aldehydes, ketones			8.54			51.4				59.9
Nitroaromatics										
Alcohols										
Amines										
Phenols, halo and nitrophenols										
Esters, amides			8.54			51.4				59.9
Mercaptans										
Carboxylic acids										
Sulfoxides										

NOTE: The MATE Comparison Value is based on the GRAV mass in the LC cut divided by the gas sample volume. For compound classes indicated by IR, the MATE comparison value is 100 percent of the GRAV concentration. For compound classes expected[65] but not identified by IR, the MATE Comparison Value is 10 percent of the GRAV concentration.

TABLE A-164. VAPOR ABOVE CHEMICAL OIL TANK, CANISTER RINSE: PRELIMINARY IR

SAMPLE: 5XR-P

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3085, 3045, 3010	S	Aromatic CH stretch
2960, 2950, 2920	W	Aliphatic CH stretch
1950-1650	W	Aromatic overtones and combinations
1595, 1500	S	Aliphatic C$\overset{\cdots}{-}$C stretch
1390, 1360	S,W	Gem-dimethyl CH bend or highly substituted aromatic cmpds
1270-960	S (sharp)	Aromatic fingerprint region
840-770	M (broad)	Substituted aromatic CH bend
725	W	

2. Unassigned weak bands: 620 cm^{-1}

3. Other remarks:

Sample predominantly aromatic hydrocarbons. Bands at 1390, 1360 and 840-770 cm^{-1} strongly suggest that alkylated derivatives are i-propyl or t-butyl α- and β-substituted naphthalenes.

TABLE A-165. VAPOR ABOVE CHEMICAL OIL TANK, CANISTER RINSE: CONCENTRATE IR

SAMPLE: 5XR-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3090, 3060-3000	S	Aromatic CH stretch
2980, 2960, 2870	M,W	Aliphatic CH stretch
1945-1665	M	Aromatic overtones/combinations
1598, 1555, 1500	S,W,S	Aromatic $C\overset{\cdots}{-}C$ Stretch
1450	W	Aliphatic CH bend
1390, 1360	S	Gem-dimethyl or t-butyl CH
1270-960	S (sharp)	Aromatic fingerprint region
825, 720	S,M	Sub. aromatic CH bend

2. Unassigned weak bands: 2290 cm^{-1} (nitrile?)

3. Other remarks:

Sample contains primarily aromatic hydrocarbons and alkylated derivatives. Bands at 1390, 1360, 825 and 720 cm^{-1} strongly suggest that these alkylated derivatives are almost entirely i-propyl or t-butyl derivatives of α- and β-sub. naphtalenes.

TABLE A-166. VAPOR ABOVE CHEMICAL OIL TANK, CANISTER RINSE: LC CUT #1 IR

SAMPLE: 5XR-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2925, 2856	S	Aliphatic CH
1733	M	Ester or oliphatic ketone
1457	M	Aliphatic CH
1376	W	Methyl C-H
1123, 1075	W	Ester or ether C-O
739	W	$-(CH_2)_n-$, $n \geq 4$ rocking or substituted aromatic
1718, 1280, 1274		CH bend

2. Unassigned weak bands: 1718, 1280, 1274

3. Other remarks:

Bands at 1733, 1123 and 1075 cm^{-1} very likely due to esters that are present.

Bands at 1280, 1274 and 739 cm^{-1} possible due to aromatic ether.

Sample appears to consist predominantly of saturated hydrocarbons and/or aliphatic esters or ketones.

TABLE A-167. VAPOR ABOVE CHEMICAL OIL TANK, CANISTER RINSE: LC CUT #2 IR

SAMPLE: 5XR-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3050	W	Aromatic CH stretch
1956-1785	W	Aromatic combination and overtone region
1593, 1505	W	Aromatic $C\overset{\cdots}{-}C$ Stretch
842	W	Substituted aromatic CH bend
780 S		

2. Unassigned weak bands: 1391, 1272, 1210, 1127, 1008, and 961 cm^{-1} (Peak at 961 cm^{-1} is of medium intensity)

3. Other remarks:

Bands in region 1956-1785 cm^{-1} and single bands at 842 and 780 cm^{-1} highly suggestive of meta- or ortho-disubstituted benzene, i.e., 3 or 4 adjacent hydrogen atoms. Sample is primarily aromatic hydrocarbons, containing few aliphatic hydrocarbons. This sample probably contains significant amounts of naphthalene.

TABLE A-168. VAPOR ABOVE CHEMICAL OIL TANK, CANISTER RINSE: LC CUT #3 IR

SAMPLE: 5XR-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2952, 2856	S	Aliphatic CH stretch
1733	S	Esters or aliphatic ketones
1459, 1376	M,W	Aliphatic CH bend
1274, 1123, 1075	M,W,W	Aromatic ester of 1° and 2° alcohols or aromatic or aliphatic ethers
808, 746	W	Substituted aromatic CH bend

2. Unassigned weak bands: 1541, 1034.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

This sample appears to be predominantly aromatic esters of 1° and/or 2° alcohols.

TABLE A-169. VAPOR ABOVE CHEMICAL OIL TANK, CANISTER RINSE: LC CUT #4 IR

SAMPLE: 5XR-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2962, 2931, 2874, 2861	S	Aliphatic CH stretch
1733	S	Ester or aliphatic ketone
1462, 1381	M	Aliphatic CH bend
1292, 1273	S	Aromatic ether or ester of aromatic acid
1122, 1071	M	Aromatic or aliphatic ether or ester of aromatic acid
744, 700	M,W	Substituted aromatic CH bend

2. Unassigned weak bands: 945, 669 .

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample appeared to contain predominantly saturated hydrocarbons and aliphatic esters of aromatic acids.

TABLE A-170. VAPOR ABOVE CHEMICAL OIL TANK, CANISTER RINSE: LC CUT #5 IR

SAMPLE: 5SR-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2963, 2931, 2878	S	Aliphatic CH
1731	S	Ester or aliphatic ketone
1488, 1456	M	Aliphatic CH bend
1377	W	Methyl CH bend
1280, 1123	S,M	Aromatic or aliphatic esters or ethers
1076	M	Ester or ether
743, 700	M,W	$-(CH_2)_n-$, $n \geq 4$ rocking or substituted aromatic CH bend

2. Unassigned weak bands: 1440, 1224, and 1038 cm^{-1}.

3. Other remarks:

Sample predominantly aliphatic esters of aromatic and aliphatic acids or aliphatic ethers.

TABLE A-171. VAPOR ABOVE CHEMICAL OIL TANK, CANISTER RINSE: LC CUT #6 IR

SAMPLE: 5XR-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3335	M(broad)	Alcoholic or phenolic OH or amide
3068	W	Aromatic CH stretch
2959, 2931, 2856	S	Aliphatic CH stretch
1732	S	Ester or aliphatic ketone
1684	M	Ketone or amide
1602	M	Aromatic C$\overset{\cdots}{-}$C stretch
1465	M	Aliphatic CH bend
1383, 1273	M	Alcohol, phenol or aromatic ether or amide CN stretch
746	W	Substituted aromatic CH bend

2. Unassigned weak bands: 1224, 1129, 1074, 1026, 965, 821, 698, 615
3. Other remarks:

Sample consists predominantly of aliphatic alcohols, amides or esters or alkylated derivatives of phenol.

TABLE A-172. VAPOR ABOVE CHEMICAL OIL TANK, CANISTER RINSE: LC CUT #7 IR

SAMPLE: 5XR-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2932, 2856	S	Aliphatic CH stretch
1739	S	Ester or aliphatic
1459	M	Aliphatic
1264, 1164, 1075	W	Ester or ether

2. Unassigned weak bands: 1678, 1602, 1561, 1376, 821, 739, 698 .
3. Other remarks:

TABLE A-173. COKE OVEN GAS

Sample Name: Coke Oven Gas

Sample Date: 12/15/77

Analysis Date: 12/15/77

C_1-C_7 HYDROCARBONS

Bulb #1

Range		# Peaks	ppm (V/V)
GC	1	1	66,190
	2	1	11,110
	3	3	1,093
	4	1	1
	5	6	43
	6	4	124
	7	0	—

Bulb #2

Range		# Peaks	ppm (V/V)
GC	1	1	66,992
	2	1	11,598
	3	3	1,159
	4	1	1
	5	6	44
	6	4	168
	7	0	—

AROMATICS (ppm, V/V)

	On-Site		RTI
	Bulb 1	Bulb 2	SS Can
Benzene	6195.5	6421.0	1667.2
Toluene	437.0	248.0	67.8
Ethyl Benzene	NA	NA	0.3
m & p Xylene	NA	NA	4.4
o Xylene	NA	NA	0.7

SULFURS (ppm, V/V)

	On-Site	
	Bulb 1	Bulb 2
H_2S (COS)	4229	5020
SO_2	—	—
CS_2	—	—

NA = No Analysis

— = Compound Not Detected

TABLE A-174. PRIMARY COOLER CONDENSATE TANK SAMPLES

Sample Date: 12/16/77

Analysis Date: 12/16/77

(Bulb #1 Only)

C_1-C_7 HYDROCARBONS

Bulb #1

Range	# Peaks	ppm (V/V)
GC 1	1	1,357
2	1	349
3	4	139
4	0	—
5	3	7
6	2	13
7	1	53

Bulb #2

Range	# Peaks	ppm (V/V)
GC 1		
2		
3		
4		
5		
6		
7		

(Bulb #1 Only)

AROMATICS (ppm, V/V)

	On-Site		RTI
	Bulb 1	Bulb 2	SS Can
Benzene	1565.6		1653.4
Toluene	160.8		178.1
Ethyl Benzene	NA		1.2
m & p Xylene	NA		37.7
o Xylene	NA		9.7

SULFURS (ppm, V/V)

	On-Site	
	Bulb 1	Bulb 2
H_2S (COS)	2350	
SO_2	—	
CS_2	—	

NA = No Analysis
— = Compound Not Detected

TABLE A-175. AMBIENT DATA SHEET

Plant Name: U.S. Steel

Location: Birmingham, Alabama

Operator: Tom Allen

Time of Sample: 15:00 12/12 to 15:00 12/13

Station Number:	1	2	3
Metered Volume cu. meter	0.258		0.275
Cyanide Catch (CN^-) μgms	16.3		1.1
Concentration ppm	0.056		0.004
μgms/std m^3	62.6		4.0

Wind Direction:

Wind came out of the southeast for the 24 hour sample period at approximately 5 mph.

Comments:

Station 1 - Chemical Lab.
2 - Mule Barn
3 - Railroad tracks

Station 2 was not in operation due to power problems at sample location.

TABLE A-176. AMBIENT DATA SHEET

Plant Name: U.S. Steel

Location: Birmingham, Alabama

Operator: Tom Allen

Time of Sample: 15:00 12/13 to 15:00 12/14

Station Number	1	2	3
Metered Volume cu. meter	0.280		0.280
Cyanide Catch (CN^-) μgms	22.0		2.5
Concentration ppm	0.069		0.008
μgms/std m^3	78.1		8.9

Wind Direction:

Wind out of Southeast for ≈ 10 hours at ≈ 9 mph.

Wind out of Southwest for ≈ 5½ hours at ≈ 6 mph.

Wind out of Northwest for ≈ 8½ hours at ≈ 5 mph.

Comments:

Station #2 down due to power problems at sampling location.

ppm calculated assuming total cyanides (CN^-) as HCN.

TABLE A-177. AMBIENT DATA SHEET

Plant Name: U.S. Steel

Location: Birmingham, Alabama

Operator: Tom Allen

Time of Sample: 15:00 12/14 to 15:00 12/15

Station Number:	1	2	3
Metered Volume cu. meter	0.289	0.215	0.289
Cyanide Catch (CN^-) µgms	4.3	0.5	2.5
Concentration ppm	0.013	0.002	0.008
µgms/std m^3	14.8	2.3	8.6

Wind Direction:

Wind from Northwest for 13 h. at ≈ 5 mph.

North for 4 h. at ≈ 3 mph; N.E. for 3 h. at ≈ 3 mph; E for 2½ h. at ≈ 3 mph; W for 1½ h.

Comments:

Wind direction varied during run: See Met. Station data sheet.

TABLE A-178. AMBIENT DATA SHEET

Plant Name: U.S. Steel

Location: Birmingham, Alabama

Operator: Tom Allen

Time of Sample: 15:00 12/15 to 12/16

Station Number:	1	2	3
Metered Volume cu. meter	0.289	0.215	0.289
Cyanide Catch (CN^-) µgms	5.8	1.0	1.5
Concentration ppm	0.018	0.004	0.005
µgms/std m^3	20.0	4.6	5.2

Wind Direction:

Wind from West for 7 hours at ≈ mph.

Wind from North for 9 hours at ≈ 2 mph.

Wind from Southwest for 8 hours at ≈ 7 mph.

Comments:

Ambient stations were taken down at 18:00 on 12/16 - 3 hour samples were not analyzed.

TABLE A-179. SASS TRAIN DATA SHEET

Plant Name: U.S. Steel

Location: Birmingham, Alabama

Date: 12/16/77

Test Performed By: F. J. Phoenix

Run Number: 7

Sampling Location: Upwind Ambient-Station #3 Railroad tracks

Pre Leak Test: 0.01

Post Leak Test: 0.02

Test Time:

Start: 19:30

Finish: 22:36

Meter Volume (c.f.):

Start: 882.05

Finish: 1883.44

Volume of Gas Sampled 1001.39

978.06 scf.

Average Gas Temperature (°F)

Ambient 57°

Sampling Location: 57°

XAD-2 Resin: 57°

Meter Box: 74°

Comments:

1. Wind out of the Southwest.

TABLE A-180. UPWIND AMBIENT TRAILER LOCATION

Sample Name: Upwind Ambient Trailer Location

Sample Date: 12/16/77

Analysis Date: 12/21/77 (at RTI)

(Bulb #1 Only)

C_1-C_7 HYDROCARBONS

Bulb #1

Range	# Peaks	ppm (V/V)
GC 1	1	2.9
2	0	—
3	0	—
4	0	—
5	0	—
6	0	—
7	0	—

Bulb #2

Range	# Peaks	ppm (V/V)
GC 1		
2		
3		
4		
5		
6		
7		

(Bulb #1 Only)

AROMATICS (ppm, V/V)

	On-Site		RTI
	Bulb 1	Bulb 2	SS Can
Benzene	0.6		0.7
Toluene	—		—
Ethyl Benzene	NA		—
m & p Xylene	NA		—
o Xylene	NA		—

SULFURS (ppm, V/V)

	On-Site	
	Bulb 1	Bulb 2
H_2S (COS)	0	
SO_2	0	
CS_2	0	

NA = No Analysis
— = Compound Not Detected

TABLE A-181. ORGANIC EXTRACT SUMMARY, UPWIND AMBIENT, XAD-2 RESIN

	Preliminary	Concentrate	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total organics mg/sm^3	5.0	2.6	0.07	1.01	0.32	0.0	0.06	0.30	0.19	1.95
TCO, mg	100	48	2.0	24.8	7.2	0.0	1.8	4.2	0.0	40.0
GRAV, mg	40	23	0.0	3.2	1.6	0.0	0.0	4.0	5.2	14.0

Category			MATE comparison value, mg/sm^3*							
			LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Aliphatic hydrocarbons				0.12						0.12
Halogenated aliphatics										0.0
Aromatic hydrocarbons				0.12	0.06			0.14		0.32
Halogenated aromatics				0.01	0.006					0.07
Heterocyclic N, O, S compounds										0.0
Sulfides, disulfides										0.0
Nitriles										0.0
Ethers								0.14	0.19	0.33
Aldehydes, ketones								0.01	0.19	0.20
Nitroaromatics								0.01		0.01
Alcohols								0.01	0.02	0.03
Amines								0.01	0.02	0.03
Phenols, halo and nitrophenols								0.01	0.02	0.03
Esters, amides								0.14	0.19	0.33
Mercaptans								0.01	0.02	0.03
Carboxylic acids								0.01	0.02	0.03
Sulfoxides								0.01	0.02	0.03

NOTE: The MATE Comparison Value is based on the GRAV mass in the LC cut divided by the gas sample volume. For compound classes indicated by IR, the MATE comparison value is 100 percent of the GRAV concentration. For compound classes expected[65] but not identified by IR, the MATE Comparison Value is 10 percent of the GRAV concentration.

TABLE A-182. UPWIND AMBIENT, XAD-2 RESIN: PRELIMINARY IR

SAMPLE: 7X-P

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2966, 2932, 2858	S	Aliphatic CH stretch
1740, 1729	S	Ester and/or aliphatic ketone
1451, 1377	M,W	Aliphatic CH bend
1266, 1116, 1099	S	Ester or atomatic ether
1076, 1029	M	Aromatic fingerprint region
798, 713	M	Substituted aromatic

2. Unassigned weak bands: 1604 cm^{-1}

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample predominantly aliphatic esters of aromatic acids.

TABLE A-183. UPWIND AMBIENT, XAD-2 RESIN: CONCENTRATE IR

SAMPLE: 7X-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3065, 3032	W	Aromatic or olefinic CH stretch
2966, 2928, 2873, 2862	S	Aliphatic CH stretch
1727	M	Saturated ketone or ester
1705	M	Aryl ketone or ester
1607, 1492	M	Aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ stretch
1453, 1376	M	Aliphatic CH bend
1261, 1113	M,W	Ester of aromatic acid, aromatic or aliphatic ether
801, 757, 708, 702	M	Substituted aromatic CH bend

2. Unassigned weak bands: 1316, 1179, 1097, 1069, 1026 cm^{-1}

3. Other remarks:

Sample contains predominantly alkylated aromatic esters (e.g. benzoates), saturated and aromatic hydrocarbons and possibly some saturated ketones and/or esters.

TABLE A-184. UPWIND AMBIENT, XAD-2 RESIN: LC CUT #1 IR

SAMPLE: 7X-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2924, 2856	S	Aliphatic CH stretch
1458	M	Aliphatic CH bend
1376	W	Isolated methyl CH bend
752, 698	W	Mono-substituted benzene

2. Unassigned weak bands: 1746, 1610 cm^{-1}.

3. Other remarks:

Sample predominantly saturated hydrocarbons. However, bend @ 1746 suggests presence of small amounts of aliphatic ketones or esters, and bends at 1610, 752 and 698 cm^{-1} suggest presence of small amounts of substituted benzene.

TABLE A-185. UPWIND AMBIENT, XAD-2 RESIN: LC CUT #2 IR

SAMPLE: 7X-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3065, 3030	M	Aromatic or olefinic CH
2965, 2924, 2871	S	Aliphatic CH stretch
1601, 1492	W,M	Aromatic $C\overset{...}{-}C$
1456	M	Aliphatic CH bend
1374	W	Isolated methyl CH bend
752, 699	M,S	Substituted aromatic CH bend

2. Unassigned weak bands: 1515, 1263, 1029, 887, 834

3. Other remarks:

Bands in C-H out-of-plane bending region for aromatics. Characteristic of mono-substituted benzene.

Sample contains only aliphatic and aromatic hydrocarbons.

TABLE A-186. UPWIND AMBIENT, XAD-2 RESIN: LC CUT #3 IR

SAMPLE: 7X-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3084, 3062, 3026, 3001	M	Aromatic or olefinic CH
2965, 2925, 2871, 2856	S	Aliphatic CH Stretch
1591, 1515	W	Aromatic C$\overset{\cdots}{-}$C ring mode
1494, 1453	M	Aliphatic CH bend
1374	W	Isolated methyl CH bend
890, 833, 778, 754	W,M,M,S	Substituted aromatic

2. Unassigned weak bands: 1729, 1263, 1098, 1031

3. Other remarks:

Sample predominantly aliphatic and aromatic hydrocarbons with a trace of ketone or ester as evidenced by very weak absorption at 1728 cm^{-1}.

TABLE A-187. UPWIND AMBIENT, XAD-2 RESIN: LC CUT #4 IR

SAMPLE: 7X-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3063	W	Aromatic or olefinic CH stretch
2959, 2929, 2856	S	Aliphatic CH stretch
1738, 1729	S	Ester or aliphatic ketone
1603, 1494, 1465	W	Aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ stretch
1453, 1380	M,W	Aliphatic CH bending
1265, 1116	S,M	Ester of aromatic acid, aromatic or aliphatic ether
794, 754, 708	W,W,S	Substituted aromatic CH bend

2. Unassigned weak bands: 1662, 1588, 1380, 1315, 1177, 1098, 1069, 1025

3. Other remarks:

Bands at 1098, 1069, 1025, 754, and 708 cm^{-1}. Suggestive of monosubstituted benzene.

Sample predominantly aromatic esters of considerable aliphatic character.

TABLE A-188. UPWIND AMBIENT, XAD-2 RESIN: LC CUT #5 IR

SAMPLE: 7X-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3020	W	Aromatic or olefinic CH
2959, 2926, 2856	S	Aliphatic CH stretch
1725	S	Ester or aliphatic ketone
1602, 1584	W	Aromatic C$\overset{\cdots}{-}$C
1462, 1454	M	Aliphatic CH bend
1380	W	Methyl CH bend
1273, 1122	S,M	Aliphatic or aromatic C-O
798, 742, 710	W,W,S	Substituted aromatic

2. Unassigned weak bands: 1175, 1071, 1026 cm^{-1}.

3. Other remarks:

Sample predominantly aliphatic and/or aryl esters. Bands for < C=O and C-O frequencies are highly suggestive or aromatic esters.

TABLE A-189. UPWIND AMBIENT, XAD-2 RESIN:
LC CUT #6 IR

SAMPLE: 7X-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3065, 3036	W	Aromatic or aliphatic CH
1726	S	Ester or aliphatic ketone
1603, 1585	M,W	Aromatic or olefinic $C\overset{\cdots}{-}C$
1456	M	Aliphatic CH bend
1380	W	Methyl CH bend
1274, 1116	S,M	Aromatic or aliphatic ether or ester or aromatic acid
758, 711	M,S	Substituted aromatic CH bend

2. Unassigned weak bands: 1515, 1174, 1069, 1028, 981 .

3. Other remarks:

Broad band at 3341 cm^{-1} due to H_2O in cell.

Sample composed primarily of aliphatic esters of aromatic acids with bands at 758 and 741 cm^{-1} being characteristic of mono-sub. benzene.

TABLE A-190. UPWIND AMBIENT, XAD-2 RESIN: LC CUT #7 IR

SAMPLE: 7X-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2965, 2930, 2859	S	Aliphatic CH stretch
1726	S	Ester or aliphatic ketone
1603	M	Olefinic or aromatic C$\overset{\cdots}{-}$C
1450	M	Aliphatic CH bend
1403	M	Olefinic CH bend
1374	M	Methyl CH bend
1274, 1109	M,S	Aromatic ester or aromatic ether and aliphatic ester
716		Olefinic C-H bend

2. Unassigned weak bands: 1556, 1027, 940 cm^{-1}

3. Other remarks:

Spectrum indicates sample is predominantly unsaturated esters, such as acrylates, maleates, etc. Bands at 1603, 1403 and 716 cm^{-1} suggests that vinyl group is _cis_-disubstituted.

TABLE A-191. UPWIND AMBIENT, CANISTER RINSE: MASS OF SAMPLE AND CONCENTRATE

	Equivalent total sample quantities			
Fraction	TCO, mg	GRAV, mg	Total, mg	Total, mg/Sm^3*
Preliminary	(----------------------data not available----)			
Concentrate	(data not available)	6.7		0.24
LC1				
LC2				
LC3				
LC4		(TCO + GRAV <15 mg, No LC)		
LC5				
LC6				
LC7				

*Standard conditions of 20° C and 760 mmHg.

TABLE A-192. UPWIND AMBIENT, CANISTER RINSE: CONCENTRATE IR

SAMPLE: 7XR-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3030	W	Aromatic CH stretch
2950, 2930, 2855	S	Aliphatic CH stretch
1725, 1715	S	Aliphatic ketone or ester
1600, 1575	W	Aromatic $C\overset{\cdots}{-}C$ stretch
1460, 1380	S,M	Aliphatic CH bend
1295, 1280	S	Ester of aromatic or α,β-unsaturated acids or aromatic ethers
1130, 1075	S	Ester of aromatic or α,β-unsaturated acids, aromatic or aliphatic ethers.

2. Unassigned weak bands: 1650, 820-760 (series of weak bands).

3. Other remarks:

This sample contains predominantly saturated and aromatic compounds. Spectrum also indicates that sample contains aliphatic esters of aromatic acids and saturated ethers.

TABLE A-193. SASS TRAIN DATA SHEET

Plant Name: U.S. Steel

Location: Birmingham, Alabama

Date: 12/16/77

Test Performed By: F. J. Phoenix

Run Number: 6

Sampling Location: Downwind Ambient-Station #1 Chem. Lab.

Pre Leak Test: 0.02

Post Leak Test: 0.02

Test Time:

Start: 14:40

Finish: 18:30

Meter Volume (c.f.):

Start: 872.52

Finish: 1876.65

Volume of Gas Sampled: 1004.13 c.f.

972.27 scf.

Average Gas Temperature (°F)

Ambient: 55°

Sampling Location: 55°

XAD-2 Resin: 55°

Meter Box: 75°

Comments:

1. Wind out of the Southeast.

TABLE A-194. DOWNWIND AMBIENT CHEM LAB SITE

Sample Name: Downwind Ambient Chem Lab Site 16:25

Sample Date: 12/16/77

Analysis Date: 12/21/77 (All Analyses at RTI)

(Bulb #1 Only)

C_1-C_7 HYDROCARBONS

Bulb #1

Range	#Peaks	ppm (V/V)
GC 1	1	3.4
2	0	—
3	0	—
4	0	—
5	0	—
6	0	—
7	0	—

Bulb #2

Range	# Peaks	ppm (V/V)
GC 1	1	3.1
2	0	—
3	0	—
4	0	—
5	0	—
6	0	—
7	0	—

(Bulb #1 Only)

AROMATICS (ppm, V/V)

	On-Site		RTI
	Bulb 1	Bulb 2	SS Can
Benzene	1.3	0.3	—
Toluene	—	—	—
Ethyl Benzene	NA	NA	—
m & p Xylene	NA	NA	—
o Xylene	NA	NA	—

SULFURS (ppm, V/V)

	On-Site	
	Bulb 1	Bulb 2
H_2S (COS)	0	0
SO_2	0	0
CS_2	0	0

NA = No Analysis

TABLE A-195. DOWNWIND AMBIENT, XAD-2 RESIN: MASS OF SAMPLE AND CONCENTRATE

	Equivalent total sample quantities			
Fraction	TCO, mg	GRAV, mg	Total, mg	Total, mg/Sm^{3*}
Preliminary	0	60.0	60.0	2.2
Concentrate	3.0	33.5	36.15	1.3
LC1				
LC2				
LC3	(TCO + GRAV <15 mg, No LC)			
LC4				
LC5				
LC6				
LC7				

*Standard conditions of 20° C and 760 mmHg.

TABLE A-196. DOWNWIND AMBIENT, XAD-2 RESIN: PRELIMINARY IR

SAMPLE: 6X-P

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2972-2856	M	Aliphatic CH stretch
1726	W	Ketone or ester
1602		Conj. olefine and/or aromatic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1445	W	Aliphatic CH bend
1260	W	Ester of aromatic acid
794	S	Substituted aromatic cmpds
699	S	

2. Unassigned weak bands: 1089, 1020, 986.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR technology.

Sample contains some saturated hydrocarbons and aromatic esters. Two sharp bands at 794 and 699 cm^{-1} suggest that aromatic cmpds are substituted such that 1,3, and 5 adjacent hydrogens are present.

TABLE A-197. DOWNWIND AMBIENT, XAD-2 RESIN: CONCENTRATE IR

SAMPLE: 6X-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3063	W	Aromatic or olefinic CH stretch
2963, 2926, 2856	S	Aliphatic CH stretch
1731	S	Ester or aliphatic ketone
1604, 1463	W,M	Aromatic C$\overset{\cdots}{-}$C
1455, 1377	M,W	Aliphatic CH bend
1262, 1095, 1020	S	Ester of aromatic acid
801, 711	S,M	Substituted aromatic CH bend

2. Unassigned weak bands: 1586, 1176, 864, 749 cm^{-1} .

3. Other remarks:

Sample contains aromatic and aliphatic esters or ethers and possibly some aliphatic ketones.

TABLE A-198. DOWNWIND AMBIENT, CANISTER RINSE: MASS OF SAMPLE AND CONCENTRATE

	Equivalent total sample quantities			
Fraction	TCO, mg	GRAV, mg	Total, mg	Total, mg/Sm^3*
Preliminary	225.0	4.0	229.0	8.3
Total GRAV		8.2		0.30
LC1				
LC2				
LC3				
LC4	(TCO + GRAV <15 mg, No LC)			
LC5				
LC6				
LC7				

*Standard conditions of 20° C and 760 mmHg.

TABLE A-199. DOWNWIND AMBIENT, CANISTER RINSE: CONCENTRATE IR

SAMPLE: 6XR-C
16XAD can Rinse #6 - downwind ambient

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2962-2858	S	Aliphatic CH
1729	S	Ester or aliphatic ketone
1599- 1584	W	Aromatic $C\overset{\cdots}{-}C$
1465	M	Aliphatic CH bend
1378	W	Methyl CH bend
1288, 1273	M,S	Ester of aromatic acid or aromatic ether
1123, 1071	M	Aromatic ester or aromatic or aliphatic ether
739	M	Substituted aromatic CH bend

2. Unassigned weak bands: 1071, 1066, 962, 812

3. Other remarks:

Bands at 2366 and 2340 cm^{-1} due to CO_2

Bands at 677 cm^{-1} due to residual methylene chloride on salt plate.

Bands at 1288 and 1273 cm^{-1} highly suggestive of an ester of aromatic acid.

Sample is predominantly aliphatic esters of aromatic acids, or possibly aromatic and/or aliphatic ethers.

TABLE A-200. AMMONIA LIQUOR, pH 2 EXTRACT: MASS OF SAMPLE, CONCENTRATE, AND LC CUTS

	Equivalent Total Sample Quantities		
Fraction	TCO, mg	GRAV, mg	Total, mg
Preliminary	8,720	6,560	15,280
Concentrate	4,670	5,030	9,700
LC1	730	1,750	2,480
LC2	3,460	880	4,340
LC3	140	680	820
LC4	210	260	470
LC5	70	0.0	70
LC6	1,860	500	2,360
LC7	0.0	80	80
Σ	6,470	4,150	10,620

TABLE A-201. AMMONIA LIQUOR, pH 2 EXTRACT: PRELIMINARY IR

SAMPLE: 8A-P

1. Major peaks and assignments

ν cm^{-1})	I	Assignments/Comments
3590, 3470	W	Free and dimeric OH stretch of phenols
3600-3000	W(broad)	Alcohol or phenolic OH stretch (polymeric)
3040, 3000	W	Aromatic CH stretch
2955, 2938, 2850	S	Aliphatic CH stretch
1660-1650	M	Diaryl ketones, carboxylate ion, or aromatic or highly conj. carboxylic acid
1455, 1380	M,W	Alkyl CH bend
845-800	W	Sub. aromatic CH bend

2. Unassigned weak bands: 1330 cm^{-1}

3. Other remarks:

Spectrum indicates that sample is predominantly alkylated phenols or alkylated derivatives of highly unsaturated or aromatic acids.

TABLE A-202. AMMONIA LIQUOR, pH 2 EXTRACT: CONCENTRATE IR

SAMPLE: 8A-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3418	W	Alcoholic or phenolic OH
3055	M	Aromatic C-H
2959, 2925, 2856	S	Aliphatic C-H
1650	M	β-diketone, diaryl ketone
1602	M	Aromatic
1459	S	Aromatic, methyl, methylene
1376	M	Aromatic, methyl, methylene
814	M	Aromatic, methyl, methylene
746	S	Aromatic, C-Cl, aliphatic

2. Unassigned weak bands: 1240.
3. Other remarks:

2363 and 2342 due to CO_2.

Sample appears to contain predominantly alkylated phenols.

TABLE A-203. AMMONIA LIQUOR, pH 2 EXTRACT: LC CUT #1 IR

SAMPLE: 8A-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2932, 2856	S	Aliphatic C-H
1465, 1376	M	Aliphatic CH bend

2. Unassigned weak bands: 725.
3. Other remarks:

Probable saturated hydrocarbon, LRMS indicative of some PNAs as well as saturated chains.

TABLE A-204. AMMONIA LIQUOR, pH 2 EXTRACT: LC CUT #1 LRMS

SAMPLE: 8A-LC1

1. Categories Present

Intensity	Category
10	PNAs
100	Aliphatic

2. Subcategories, Specific compounds

Intensity	Subcategory/Compounds
10	perylene, benzpyrene, m/e 252
10	chrysene, triphenylene, m/e 228
10	anthracene, phenanthracene, m/3 178

3. Other

Intensity	Comments
100	Clusters to high intensity peaks every 14 amu. From ∿125 amu to ∿55amu. Suggestive of saturated chains.

TABLE A-205. AMMONIA LIQUOR, pH 2 EXTRACT: LC CUT #2 IR

SAMPLE: 8A-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3055	S	Aromatic C-H, -CH$_2$-halogen
2959, 2925, 2870	S	Aliphatic C-H
1931	W	Aromatic
1808	W	Aromatic
1733	W	Aromatic
1602	M	Aromatic
1458	S	Aliphatic CH bend
1376	M	Methyl CH bend
1315	M	Aromatic
1246	M	Aromatic
1911	M	Aromatic
1081, 1033, 958	M	Aromatic
833, 732	S	Aromatic, C-Cl, aliphatic

2. Unassigned weak bands:
3. Other remarks:

Probable mono-substituted alkyl aromatic.

TABLE A-206. AMMONIA LIQUOR, pH 2 EXTRACT: LC CUT # 2 LRMS

SAMPLE: 8A-LC2

1. Categories Present

Intensity	Category
100	PNAs
10	PNAs

2. Subcategories, Specific Compounds

Intensity	Subcategory/Compounds
100	Pyrene, m/e 202
10	Perylene, benzpyrene, m/e 252
10	Chrysene, triphenylene, m/e 228
10	Anthracene, phenanthrene, m/e 178
10	Acenaphthylene ? m/e 152
1	Anthracene ? m/e 276

3. Other

Intensity	Comments

TABLE A-207. AMMONIA LIQUOR, pH 2 EXTRACT:
LC CUT #3 IR

SAMPLE: 8A-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3055	S	Aromatic C-H, -CH_2-halogen
2925	W	Aliphatic C-H
1650	W	Unsaturated aromatic
1602	M	Aromatic
1452	S	Aromatic
1191	M	Aromatic
883	M	Aromatic
842	S	Aromatic
815	S	Aromatic
773	S	Aromatic
746	S	Aromatic

2. Unassigned weak bands: 1924, 1801.

3. Other remarks:

   PNA hydrocarbons; confirmed by LRMS

TABLE A-208. AMMONIA LIQUOR, pH 2 EXTRACT: LC CUT #3 LRMS

SAMPLE: 8A-LC3

1. Categories present

Intensity	Category
100	PNAs

2. Subcategories, Specific Compounds

Intensity	Subcategory/Compounds
100	Perylene, benzpyrene, m/e 252
100	Chrysene, triphenylene, m/e 228
100	Pyrene, m/e 202
10	Anthracene, phenanthrene, m/e 178

3. Other

Intensity	Comments
100	High molecular weight PNAs @ m/e 404, 378, 352, 326, 302, 276, Compatible with IR.

TABLE A-209. AMMONIA LIQUOR, pH 2 EXTRACT: LC CUT #4 IR

SAMPLE: 8A-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3425	M	Alcoholic or phenolic OH
3055	W	Aromatic C-H
1650	W	β-diketone unstaurated C-H carboxylic acid, diaryl ketone
1452	S	Aliphatic C-H
1328	M	Aliphatic C-H, phenol, acid
1239	M	Aliphatic C-H, phenol, acid or alcohol
746	S	CH_3, C-Cl, Aromatic
725	S	CH_3, C-Cl, aromatic

2. Unassigned weak bands:

3. Other remarks:

2390, 2370, due to CO_2.

TABLE A-210. AMMONIA LIQUOR, pH 2 EXTRACT: LC CUT #4 LRMS

SAMPLE: 8A-LC4

1. Categories present

Intensity	Category
100-10	Amines

2. Subcategories, Specific Compounds

Intensity	Subcategory/Compounds
10-100	Polyaromatic amines, m/e 341, 317 291, 267, 241, 217

3. Other

Intensity	Comments

TABLE A-211. AMMONIA LIQUOR, pH 2 EXTRACT
LC CUT #5 IR

SAMPLE: 8A-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3384	M	OH
3055	M	Aromatic C-H
2932	S	Aliphatic C-H
2856	M	Aliphatic C-H
1719	W	Ketone, ester
1602	M	Aromatic
1458	S	Aromatic
1376	M	Aromatic
1273	M	CH_3-
821	M	
746	S	Phenyl, C-Cl, aliphatic

2. Unassigned weak bands: 2226, 1917.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Substituted phenol probable. Bands at 2363 cm^{-1} and 2239 cm^{-1} due to CO_2.

TABLE A-212. AMMONIA LIQUOR, pH 2 EXTRACT: LC CUT #6 IR

SAMPLE: 8A-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3280	S	Aromatic C-H
3199	S	Aromatic C-H
3055	S	Aromatic C-H
2925	S	Aliphatic C-H
2863	M	Aliphatic C-H
1650	S	β-diketone, carboxylate, diaryl ketone
1596	S	Substituted phenyl
1459	S	Substituted phenyl
1280	S	Ester, ether
835	M	Aromatic C-H
752	S	C-Cl, aromatic C-H, aliphatic

2. Unassigned weak bands: 2226.

3. Other remarks:

LRMS supports aromatic nature of compounds responsible for this spectrum. Probably heterocyclic amines.

TABLE A-213. AMMONIA LIQUOR, pH 2 EXTRACT: LC CUT #6 LRMS

SAMPLE: 8A-LC6

1. Categories present

Intensity	Category
10-100	Amines

2. Subcategories, Specific Compounds

Intensity	Subcategory/Compounds
10-100	Amines, m/e 303, 279, 253, 229, 203 195, 179, 159, 145. These materials show ion characteristic of condensed aromatic rings.

3. Other:

Intensity	Comments
10-100	m/e 184, 122

TABLE A-214. AMMONIA LIQUOR, pH 2 EXTRACT: LC CUT #7 IR

SAMPLE: 8A-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2970	S	Aliphatic C-H (stretching)
2925	S	Aliphatic C-H (stretching)
2875	M	Aliphatic C-H (stretching)
1740	S	Ester or aliphatic ketone
1431	M	Aliphatic C-H (bending)
1376	M	Aliphatic C-H (bending)
1239	S	Ester C-O
1123	M	Ester C-O
1082	M	Ester C-O
1027	M	Ester C-O
739	M	C-Cl, aromatic C-H, aliphatic
698	M	C-Cl, aromatic C-H, aliphatic
616	M	C-Cl, aromatic C-H, aliphatic

2. Unassigned weak bands:

3. Other remarks:

   Probable ester.

TABLE A-215. AMMONIA LIQUOR, pH 2 EXTRACT: LC CUT #5 LRMS

SAMPLE: 8A-LC7

1. Categories Present

Intensity	Category
10	PNAs

2. Subcategories, Specific Compounds

Intensity	Subcategory/Compounds
10	perylene, benzpyrene, m/e 252
	triphenylene, chrysene, m/e 228
	pyrene, m/e 202
	anthracene, phenathrene, m/3 178

3. Other

Intensity	Comments
100	m/e 256?
	No significant ion intensity >∿256

TABLE A-216. AMMONIA LIQOUR, pH 12 EXTRACT: MASS OF SAMPLE, CONCENTRATE, AND LC CUTS

Equivalent Total Sample Quantities			
Fraction	TCO, mg	GRAV, mg	Total, mg
Preliminary	2,000	1,156	3,156
Concentrate	1,278	1,385	2,663
LC1	0	138	138
LC2	105	20	125
LC3	175	60	235
LC4	50	60	110
LC5	0	0	0
LC6	1,320	690	2,010
LC7	0	50	50
Σ			2,670

TABLE A-217. AMMONIA LIQUOR, pH 12 EXTRACT: PRELIMINARY IR

SAMPLE: 8B-P

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3500 - 3150	Broad	Unresolved band due to NH stretch of amines and anides
3090, 3020	M	Aromatic or olefinic CH stretch
2920, 2918, 2860	M	Diphatic CH stretch
1725	S	Ester or diphatic ketone
1650	S	Amide I band
1615 - 1590	S (broad)	Substituted aromatic C-C or NH bend of 1° amine
1370	W	Aliphatic CH bend
1240, 1120	S	Ester of aromatic acid, CN stretch of amines or anides, alcohol or aromatic ether
690, 640	M	Substituted aromatic CH bend

2. Unassigned weak bands: 920 cm^{-1} .

3. Other remarks:

Sample appears to be predominantly aliphatic amides and ketones, but only some substituted benzene compounds.

TABLE A-218. AMMONIA LIQUOR, pH 12 EXTRACT: CONCENTRATE IR

SAMPLE: 8B-C

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3600		"Free" OH of alcohol or phenol
3500-2900	(broad)	OH and/or NH stretch of alcohols, amines, and anides
3030, 3000		Aromatic or olefinic CH stretch
2955, 2930, 2875, 2850		Diphatic CH stretch
1725		Ester or aliphatic ketone
1660		Amide I band
1595, 1500		Aromatic C-C and amino NH bend
1470, 1385		Aliphatic CH bend
1250-1080		CH stretch for amines and anides, C-O stretch of alcohol, C-C-O stretch of aromatic esters, or C-O-C stretch of ethers
840 - 730	(broad)	Amine and anide NH bend
810		Substituted aromatic CH bend

2. Unassigned weak bands: 1510, 1340, 1000, 950 cm^{-1} .

3. Other remarks:

Bands at 1610, 1605, 1595, and 1510 cm^{-1} probably arising from NH stretching of 1° and 2° amides and amines.

Sample predominantly aromatic and aliphatic amines and amides, but also containing some alcohols aliphatic ketones, esters of aromatic acids, and/or aromatic or aliphatic ethers.

TABLE A-219. AMMONIA LIQUOR, pH 12 EXTRACT: LC CUT #1 IR

SAMPLE: 8B-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2960, 2926, 2852	S	Alkane
1462, 1377, 1281	M	Alkane
1037	M	Alkane

2. Unassigned weak bands: 1735.
3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample consisted of saturated hydrocarbons and saturated ethers.

TABLE A-220. AMMONIA LIQUOR, pH 12 EXTRACT:
LC CUT #2 IR

SAMPLE: 8B-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3055	M	Aromatic C-H, $-CH_2$-halogen
2959, 2925, 2856	S	Aliphatic C-H
1452	M	Aromatic, aliphatic
1376	W	Aliphatic
833, 842, 815, 773	M	Aliphatic
732	S	Aliphatic, C-Cl, aliphatic

2. Unassigned weak bands: 1938, 1726.
3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

2362 and 2342 due to CO_2. Probable PNA hydrocarbon. Sample contains alkylated aromatic hydrocarbons.

TABLE A-221. AMMONIA LIQUOR, pH 12 EXTRACT: LC CUT #3 IR

SAMPLE: 8B-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3053	W	Aromatic C-H, $-CH_2$-halogen
2926, 2853	S	Aliphatic C-H
1728	W	Ester or aliphatic ketone
1668	W	Alkene
1456	M	Aromatic, methyl, methylene
1238	W	Ester, ether
815	M	Aromatic, C-Cl
749	M	Aromatic, C-Cl

2. Unassigned weak bands: 1377, 881, 640.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

2363 and 2339 due to CO_2. Specific PNA's identified by LRMS.

TABLE A-222. AMMONIA LIQUOR, pH 12 EXTRACT: LC CUT #3 LRMS

SAMPLE: 8B-LC3

1. Categories present

Intensity	Category
100	PNA's

2. Subcategories, specific compounds

Intensity	Subcategory/Compounds
100	Naphthalene, M/e 128
10	Anthracene, phenanthrene M/e 178
10	Pyrene M/e 202
10	Chrysene, triphenylene M/e 228
100	Perylene, benzpyrene M/e 252
100	Anthanthrene, M/e 276

3. Other

Intensity	Comments
100 @ high probe temperatures	Ions at M/e 476, 474, 450, 426, 424, 400 376, 374, 352, 350, 326, 302. Overall ms pattern strongly indicative of high molecular weight PNA's. PNA assignments supported by IR.

TABLE A-223. AMMONIA LIQUOR, pH 12 EXTRACT: LC CUT #4 IR

SAMPLE: 8B-LC4

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3459	M	OH/NH
3062	M	Aromatic C-H,-CH_2-halogen
2973, 2918	S	Aliphatic C-H
2856	M	Aliphatic C-H
1725	W	Ester, ketone
1602	W	Aromatic
1431, 1335	S	Aromatic, methyl
1239	S	Ester, ether, amine
1095	M	Aromatic
965	M	Aromatic
746, 615	S	Aromatic, C-Cl , aliphatic

2. Unassigned weak bands: 1198, 698 .

3. Other remarks:

This sample possessed less mass than taht required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Probable aromatic amine or alcohol. LRMS more consistent with amines.

TABLE A-224. AMMONIA LIQUOR, pH 12 EXTRACT: LC CUT #4 LRMS

SAMPLE: 8B-LC4

1. Categories present

Intensity	Category

2. Subcategories, Specific Compounds

Intensity	Subcategory/Compounds

3. Other

Intensity	Comments
	No significant ion intensity $>\sim$420 amu (70 eV). Many prominent ions throughout spectra of odd M/e (70 eV and 20 eV). Consistent with amine structures as indicated by IR. No PNA's present.

TABLE A-225. AMMONIA LIQUOR, pH 12 EXTRACT: LC CUT #5 IR

SAMPLE: 8B-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3600-3200	W(broad)	Alcohol or phenolic OH
2959, 2932, 2856	S	Aliphatic CH stretch
1733	M	Ester or aliphatic ketone
1602	W	Aromatic C-C
1459, 1438	M	Aliphatic CH bend, aromatic
1249, 1102	M	Ester or aromatic acid, alcohol, ether
746, 698	W	Substituted aromatic CH bend

2. Unassigned weak bands: 972, 855 cm^{-1}.

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Probable alcohols and esters of aromatic acids.

TABLE A-226, AMMONIA LIQUOR, pH 12 EXTRACT: LC CUT #5 LRMS

SAMPLE: 8B-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2932, 2856	S	Aliphatic C-H
1733	M	Ketone/ester
1602	W	
1459, 1328	M	$-CH_2-$
1438, 1246	S	Alkane
1328, 1102	M	Alkane
972	M	Aromatic fingerpoint
835	W	Aromatic
746	W	Aromatic

2. Unassigned weak bands: 698

3. Other remarks:

TABLE A-227. AMMONIA LIQUOR, pH 12 EXTRACT: LC CUT #6 IR

SAMPLE: 8B-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3343, 3144	M	OH, NH
3062	S	Aromatic C-H
2932	S	Aliphatic C-H
2863	M	Aliphatic C-H
2713, 2610	M	H-bonded OH, NH
1733	M	Ketone, ester
1595	S	Aromatic, C$\overset{\cdots}{-}$C
1507, 1472	S	Aromatic, methyl, methylene
1376	M	Methyl CH bend
1239	S	Ester, ether, CN stretch of aromatic amine
787	S	

2. Unassigned weak bands:

3. Other remarks:

Sample predominantly aromatic amines, esters of aromatic acids, or diphatic or aromatic ethers.

TABLE A-228. AMMONIA LIQUOR, pH 12 EXTRACT: LC CUT #6 LRMS

SAMPLE: 8B-LC6

1. Categories Present

Intensity	Category
100	Amines? M/e 401 (possibly halogenated), 377 [ionizing voltage = 20 eV]

2. Subcategories, Specific Compounds

Intensity	Subcategory/Compounds

3. Other

Intensity	Comments
	M/e 327, 303, 277, 168, 149, 129 [ionizing voltage = 70 eV] Data not sufficient for subcategory or compound assignment.

TABLE A-229. AMMONIA LIQUOR, pH 12 EXTRACT: LC CUT #7 IR

SAMPLE: 8B-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2932	S	Aliphatic C-H
2856	M	Aliphatic C-H
1733	S	Ketone, ester
1616	M	Aromatic C$\overset{\cdots}{-}$C
1459	M	Aromatic, methyl, methylene
1383	M	Methyl CH bend
1246	M	Ester, ether
1171	M	Ester, ether
746	W	Aromatic, C-Cl, diphatic

2. Unassigned weak bands: 3596 broad .

3. Other remarks:

   Probable ester.

TABLE A-230. AMMONIA LIQUOR, pH 12 EXTRACT: LC CUT #7 LRMS

SAMPLE: 8B-LC7

1. Categories Present

Intensity	Category
1-10	PNA's

2. Subcategories, Specific Compounds

Intensity	Subcategory/Compounds
10	Perylene, benzpyrene, M/e 252
10	Chrysene, triphenylene, M/e 228
10	Pyrene, M/e 202

3. Other

Intensity	Comments
	No significant ion intensity >∿M/e 300 with exception of one ion at M/e 368.
100	M/e 168, 144, 130, 118 (?)
10	M/e 182

TABLE A-231. ORGANIC EXTRACT SUMMARY, BIOLOGICAL TREATMENT PLANT SLUDGE, pH 7 EXTRACT

	Preliminary	Concentrate	LC1	LC2	LC3	LC4	LC5	LC5	LC7	[illegible]
Total Organics, mg/l	23.8	7.8	2.1	0.50	0.60	0.2	0.05	2.7	0.3	6.5
TCO, mg	135	3.0	0	0	0	0	0	0	0	0
GRAV, mg	45	56.0	16.0	3.6	4.4	1.6	0.4	20.8	2.4	49.2
Category			MATE Comparison Value, mg/l							
Aliphatic hydrocarbons			2.1							2.1
Halogenated aliphatics			0.2							0.2
Aromatic hydrocarbons			2.1	0.5	0.6	0.2	0.05	2.7	0.3	6.45
Halogenated aromatics				0.05	0.06	0.02				0.13
Heterocyclic N, O, S compounds						0.02	0.005			0.025
Sulfides, disulfides						0.02	0.005			0.025
Nitriles						0.02	0.005			0.025
Ethers					0.6	0.02	0.005	2.7		3.32
Aldehydes, ketones					0.6	0.2	0.005	2.7		3.5
Nitroaromatics							0.005	0.3		0.30
Alcohols							0.005	2.7	0.3	3.00
Amines							0 005	0.3		0.30
Phenols, halo and nitrophenols						0.2		2.7	0.3	3.2
Esters, amides					0.6	0.2		2.7	0.03	3.5
Mercaptans								0.3	0.03	0.33
Carboxylic acids								2.7	0.03	2.73
Sulfoxides									0 03	0.03

Note: The MATE Comparison Value is based on the GRAV mass in the LC cut divided by the sample volume. For compound classes indicated by IR, the MATE comparison value is 100 percent of the GRAV concentration. For compound clases expected but not indicated by IR, the MATE comparison value is 10 percent of the GRAV concentration.

TABLE A-232. BIOLOGICAL TREATMENT PLANT SLUDGE, pH 7 EXTRACT: PRELIMINARY IR

SAMPLE: 12P biological sludge; preliminary

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3058	W	Aromatic CH or olefinic CH
2960-2930	S	Aliphatic CH
2857	S	Aliphatic and/or aldehydic CH
1709	W	Ketone, ester, aldehyde
1642-1550	M	Aromatic or olefinic C=C
1465	M	Aliphatic CH (methylene) or aromatic C=C
1380	W	Aliphatic CH (methylene) or α-naphthalene
1282-1240	W	Aromatic ether or ester C-O
752	W	Aromatic CH

2. Unassigned weak bands: 831, 787, 697 cm^{-1}.

3. Other remarks:

Inverted bands at 2370-2340 cm^{-1} due to CO_2. Bands around 700-850 cm^{-1} suggestive of 3-, 4-, and 5- adjacent aromatic CH.

TABLE A-233. BIOLOGICAL TREATMENT PLANT SLUDGE, pH 7 EXTRACT: CONCENTRATE IR

SAMPLE: 12-C biological sludge, pH 7.0 extract concentrated sample

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3055	W	Aromatic CH
2959-2856	S	Aliphatic and aldehydic CH
1712	M	Ketone, ester
1657	M	Olefine (conj.) or aromatic C=C
1595	M	Aromatic ring (C=C)
1458	M	Aliphatic or aromatic CH
1376	M	Aliphatic CH (methyl)
1273 - 1239	W	Aromatic ether, or ester
752	M	(CH_2) rocking for $n \geq 4$ or aromatic CH

2. Uassigned weak bands: 821, 787, 691 cm^{-1}

3. Other remarks:

Bands at 2363 and 2342 cm^{-1} are due to presence of CO_2 in cell, inadequate purging.

Probable compounds and alkylated derivatives.

TABLE A-234. BIOLOGICAL TREATMENT PLANT SLUDGE, pH 7 EXTRACT LC CUT #1 IR

SAMPLE: 12-LC1

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
2959, 2927, 2857	S	Aliphatic CH stretch
1463	M	Aliphatic CH methyl and methylene
1377	W	Aliphatic C-C methyl
720, 677	W	Aromatic CH bend

2. Uassigned weak bands: 2724, 1150 cm^{-1}

3. Other remarks;

Bands at 2363 and 2342 cm^{-1} due to CO_2. Band at 676 cm^{-1} likely due to residual CH_2Cl_2 left on plate.

Probable saturated hydrocarbons, with trace amounts of aromatic compounds.

TABLE A-235. BIOLOGICAL TREATMENT PLANT SLUDGE, pH 7 EXTRACT: LC CUT #2 IR

SAMPLE: 12-LC2

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3013	W	aromatic or olefinic CH
2959 - 2863	S	aliphatic CH
1602	W	aromatic C-C
1458	M	aliphatic C-H bend
1376	M	methyl CH bend
814, 746	W	substituted aromatic

2. Unassigned weak bands:

3. Other remarks:

Bands at 2365 and 2340 cm^{-1} due to CO_2. Splitting pattern at 846, 814 and 746 cm^{-1} highly suggestive of meta-substituted benzene.

Probable alkylated aromatic hydrocarbons.

TABLE A-236. BIOLOGICAL TREATMENT PLANT SLUDGE, pH 7 EXTRACT: LC CUT #3 IR

SAMPLE: 12-LC3

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3048	S	aromatic or olefinic CH stretch
2952 - 2924	S	aliphatic C-H stretch
2856	S	aliphatic C-H stretch
1725	W	ketones, esters
1602	S	aromatic or olefinic C-C
1445, 1376	S,M	aliphatic CH bend
1259	M	aromatic ether or ester
1184, 1150	M	ether, ester
883, 842, 814, 741	S	substituted aromatic CH bend

2. Unassigned weak bands: 1917, 1026, 951

3. Other remarks:

Broad weak band at 3400 - 3200 cm^{-1} suggests alcohols or phenols. Probable alkylated aromatic hydrocarbons.

TABLE A-237. BIOLOGICAL TREATMENT PLANT SLUDGE, pH 7 EXTRACT: LC CUT #4 IR

SAMPLE: 12-LC4 Biological Sludge, pH 7.0 extract

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3418	M	OH or NH stretch (broad)
3048	M	aromatic C-H
2959, 2856	S	aliphatic C-H
1718	M	ketone, ester
1595	M	aromatic or olefin C=C
1458, 1438	S	methylene (doublet)
1376	M	$-CH_3$
876, 828, 807	M	aromatic C-H
746	S	aromatic C-H

2. Unassigned weak bands: 1328, 1266, 1239, 1177, 1033, 951

3. Other remarks:

Bands at 2363 - 2340 cm^{-1} are due to presence of CO_2 in cell.

Spikes about 1600 - 1800 are due to presence of water vapor in cell.

Probable alkylated aromatic hydrocarbons.

TABLE A-238. BIOLOGICAL TREATMENT PLANT SLUDGE, pH 7 EXTRACT: LC CUT #5 IR

SAMPLE: 12-LC5

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3048	W	aromatic or olefinic CH
2959, 2924, 2856	S	aliphatic CH
1602	M	aromatic C$\overset{\cdots}{-}$C stretch
1451	M	aliphatic CH bend
1375	W	methyl CH bend
883, 821, 752	W,W,S	substituted aromatic

2. Unassigned weak bands: 2219, 1280, 1184 cm^{-1}

3. Other remarks:

This sample possessed less mass than that required by the Level 1 criteria for IR analysis. A spectrum of acceptable quality was obtained by using Fourier Transform IR techniques.

Sample contains only saturated, unsaturated and/or aromatic hydrocarbons. Possibly some ketones or esters present as evidenced by small absorption at 1712 cm^{-1}.

TABLE A-239. BIOLOGICAL TREATMENT PLANT SLUDGE, pH 7 EXTRACT: LC CUT #6 IR

SAMPLE: 12-LC6

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3281	broad (M)	alcoholic, phenolic or acid OH
3055		aromatic OR olefinic CH
2959, 2931, 2856	S	aliphatic CH
1712	S	ketone or ester
1657	S	carboxylic acid or ketone
1602	S	aromatic or olefinic $C\overset{\cdots}{-}C$
1451, 1376	W	aliphatic CH bend
1280	M	acid, ester of aromatic acid
1191	M	ether, alcohol or phenol
810, 752	M	substituted aromatic CH

2. Unassigned weak bands: 1081, 1033, 835, 615 cm^{-1}

3. Other remarks:

Sample predominantly phenolic compounds, or carboxylic acids.

TABLE A-240. BIOLOGICAL TREATMENT PLANT SLUDGE, pH 7 EXTRACT: LC CUT #7 IR

SAMPLE: 12-LC7

1. Major peaks and assignments

ν (cm^{-1})	I	Assignments/Comments
3550 - 3000	broad	phenol or alcoholic OH stretch
3061	S	aromatic or olefinic
2931, 2856	S	aliphatic CH stretch
1602	S	aromatic or olefinic $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$
1280, 1122, 1040	M	alcohol or phenol
828, 760	W	substituted aromatic CH bend

2. Unassigned weak bands: 1664, 1726 cm^{-1}

3. Other remarks:

Sample predominantly alcohol or phenolic compounds.

TABLE A-241. TOTAL CHROMATOGRAPHABLE ORGANICS (TCO) ANALYSIS OF SAMPLES

Sample	Preliminary Sample		Concentrate Sample		Volume put on LC Column, ml	Total TCO mass in LC cuts, mg[a]							
	Volume (ml)	TCO (mg)	Volume (ml)	TCO (mg)		LC 1	LC 2	LC 3	LC 4	LC 5	LC 6	LC 7	Total
Froth Flotation Separator, XAD Resin	2,990	18,538	250	13,175	1.0	0.0	48.0	0.8	0.1	4.8	0.0	0.0	53.7
Final Cooler CT, XAD Resin	3,370	6,066	60	1,410	2.0	0.0	34.0	0.7	1.1	0.9	6.2	0.0	42.9
Tar Storage Tank, XAD Resin	3,310	6,620	100	6,090	1.0	1.8	42.0	3.5	0.8	0.4	4.5	0.0	53.0
Tar Decanter Vapor, XAD Resin	3,090	31,518	750	33,675	1.0	0.0	14.7	14.9	0.8	0.1	0.8	0.0	31.3
Chemical Oil Tank, XAD Resin	3,220	26,726	500	28,800	1.0	0.3	14.9	17.7	0.0	0.2	6.0	0.0	39.1
Downwind Ambient, XAD Resin	2,750	0	5.0	3.0	-	-	-	-	INSUFFICIENT MASS--NO LC			-	-
Upwind Ambient, XAD Resin	1,000	100	5.0	4.8	2.5	1.0	12.4	3.6	0.0	0.9	2.1	0.0	20.0
Froth Flotation separator, Can. Rinse	150	360	b	b	174.5/85.5[b]	0.0	1.0	0.2	0.0	0.0	0.7	0.0	1.9
Final Cooler Ct. Can. Rinse	60	138	b	b	743.4/61.3[b]	-	-	-	INSUFFICIENT MASS--NO LC			-	-
Tar Storage Tank, Can. Rinse	150	1,545	b	b	6,500/103.9[b]	2.0	30.0	37.4	0.2	0.0	2.0	0.0	71.6
Tar Decanter Vapor, Can Rinse	210	8,190	b	b	22,120/90.4[b]	0.0	88.3	1.0	0.0	0.0	5.1	0.0	94.4
Chemical Oil Tank, Can. Rinse	200	2,480	b	b	0	15.3	65.6	17.4	0.0	0.0	4.2	0.0	102.5
Downwind Ambient, Can. Rinse	75	225	b	b	0	-	-	-	INSUFFICIENT MASS--NO LC			-	-
Upwind Ambient, Can. Rinse		not available			-	-	-	-	INSUFFICIENT MASS--NO LC			-	-
Ammonia Liquor, pH2	800	8,720	100	4,670	1.0	7.3	34.6	1.4	2.1	0.7	18.6	0.0	64.7
Ammonia Liquor, pH12	800	2,000	25	1,278	0.5	0.0	2.1	3.5	1.0	0.0	26.4	0.0	33.0
Final Cooler CT hot well, pH2	800	2,160	10	1,463	0.5	0.0	30.0	0.0	4.2	1.1	28.7	0.0	64.0
Final Cooler CT hot well, pH12	800	720	10	660	1.0	0.0	2.9	0.0	2.6	1.0	41.7	0.0	48.2
Final Cooler CT cold well, pH2	800	1,360	10	862	0.5	0.0	10.2	0.0	1.2	3.4	28.1	0.0	42.9
Final Cooler CT cold well, pH12	800	480	10	356	2.0	0.0	0.1	0.0	1.5	0.9	47.8	0.0	50.3
Tar Decanter condensate, pH2	150	1,545	10	923	0.5	0.0	5.4	3.7	1.9	2.1	29.8	0.0	42.9
Tar Decanter condensate, pH12	150	345	10	338	2.0	0.0	1.3	0.6	0.7	3.1	41.5	0.0	47.2
Bio. plant sludge, pH7	450	135	10	3	5.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

[a] TCO mass is ratioed back to original sample by multiplying TCO mass in an LC cut by (Concentrate Volume/Volume put on column). Blanks have been subtracted from this data.

[b] Total canister rinse samples taken to dryness after preliminary analysis. Sample placed on LC column was a weighed fraction of this dry sample. The ratio total sample/sample on column is given in the column titled "Volume put on LC column." The TCO mass in an LC cut can be ratioed back to the original sample by multiplying by the above ratio.

TABLE A-242. RAW GRAV ANALYSIS DATA

Sample	Preliminary Sample Volume (ml)	Preliminary Sample GRAV (mg)	Concentrate Sample Volume (ml)	Concentrate Sample GRAV (mg)	Volume on Column ml	Liquid Chromatography Work (mass in mg)[(a)] LC 1 GRAV	LC 1 Blank	LC 1 Cor-rected	LC 2 GRAV	LC 2 Blank	LC 2 Cor-rected	LC 3 GRAV	LC 3 Blank	LC 3 Cor-rected	LC 4 GRAV	LC 4 Blank	LC 4 Cor-rected	LC 5 GRAV	LC 5 Blank	LC 5 Cor-rected	LC 6 GRAV	LC 6 Blank	LC 6 Cor-rected	LC 7 GRAV	LC 7 Blank	LC 7 Cor-rected
Froth Flotation Separator, XAD Resin	2,990	40	250	394.5	1.0	0.5	0.5	0.0	0.2	0.5	-0.3	0.4	0.4	0.0	0.3	0.3	0.0	0.3	0.3	0.0	0.2	0.6	-0.4	0.4	0.5	-0.1
Final Cooler CT, XAD Resin -	3,370	60	60	282	2.0	0.3	0.5	-0.2	0.5	0.5	0.0	0.3	0.4	-0.1	0.2	0.3	-0.1	0.2	0.3	-0.1	0.6	0.6	0.0	0.4	0.5	-0.1
Tar Storage Tank, XAD Resin	3,310	100	100	2,540	1.0	0.1	0.5	-0.4	0.6	0.5	0.1	0.2	0.4	-0.2	0.4	0.3	0.1	0.5	0.3	0.2	0.3	0.6	-0.3	0.8	0.5	0.3
Tar Decanter Vapor, XAD Resin	3,090	20,080	750	21,840	1.0	0.4	0.3	0.1	0.9	0.3	0.6	0.5	0.5	0.0	0.1	0.5	-0.4	0.3	0.3	0.0	0.7	0.4	0.3	0.2	0.4	[illegible]
Chemical Oil Tank, XAD Resin	3,220	3,360	500	5,730	1.0	0.3	0.3	0.0	0.3	0.3	0.0	0.3	0.5	-0.2	0.3	0.5	-0.2	0.2	0.3	-0.1	0.4	0.4	0.0	0.3	0.4	-0.1
Downwind Ambient, XAD Resin	2,750	60	5.0	33.5		INSUFFICIENT MASS--NO LC																				
Upwind Ambient, XAD Resin	1,000	40	5.0	23 (b)	2.5 (b)	0.3	0.3	0.0	1.1	0.3	0.8	0.9	0.5	0.4	0.3	0.5	-0.2	0.2	0.3	-0.1	1.4	0.4	1.0	1.7	0.4	[illegible]
Froth Flotation Separator, Can. Rinse	150	493	0	174.5	85.5 mg	4.6	0.0	4.6	3.9	0.2	3.7	3.9	0.3	3.6	1.5	0.3	1.2	1.0	0.1	0.9	6.1	0.4	5.7	1.6	0.3	[illegible]
Final Cooler CT Can. Rinse	60	16	0	5.2		INSUFFICIENT MASS--NO LC																				
Tar Storage Tank, Can. Rinse	150	109[c]	0	743.4	61.3 mg	0.3	0.0	0.3	1.5	0.2	1.3	0.7	0.4	0.3	0.2	0.1	0.1	0.3	0.3	0.0	0.6	0.7	-0.1	0.2	0.3	-0.1
Tar Decanter Vapor, Can Rinse	210	1,764	0	6,500	103.9 mg	0.4	0.0	0.4	19.3	0.2	19.1	0.6	0.4	0.2	0.2	0.1	0.1	0.6	0.3	0.3	0.8	0.7	0.1	0.5	0.3	0.2
Chemical Oil Tank, Can. Rinse	200	8,960	0	22,120	90.4 mg	0.2	0.0	0.2	13.7	0.2	13.5	0.3	0.4	-0.1	1.6	0.1	1.5	0.3	0.3	0.0	0.3	0.7	-0.4	0.1	0.3	-0.2
Downwind Ambient, Can. Rinse	75	4	0	8.2		INSUFFICIENT MASS--NO LC																				
Upwind Ambient, Can. Rinse						NOT AVAILABLE--SAMPLE COST																				
Ammonia Liquor, pH2	800	6,560	100	5,030	1.0	7.0	-0.2	7.0	4.6	0.2	4.4	3.6	0.2	3.4	1.3	0.0	1.3	0.4	0.4	0.0	3.4	0.9	2.5	0.6	0.2	0.4
Ammonia Liquor, pH12	800	1,156	25	1,385	0.5	1.1	0.2	1.1	0.4	0.2	0.2	0.8	0.2	0.6	0.6	0.0	0.6	0.2	0.4	-0.2	7.8	0.9	6.9	0.7	0.2	0.5
Final Cooler CT hot well, pH2	800	192	10	362	0.5	0.5	-0.2	0.5	0.6	0.2	0.4	0.3	0.2	0.1	0.3	0.0	0.3	0.2	0.4	-0.2	2.5	0.9	1.6	0.5	0.2	0.3
Final Cooler CT hot well, pH12	800	80	10	250	1.0	0.1	0.2	-0.1	0.2	0.4	-0.2	0.3	0.2	0.1	0.3	0.0	0.3	0.1	0.1	0.0	7.7	0.4	7.3	0.1	0.2	-0.1
Final Cooler CT cold well, pH2	800	160	10	358	0.5	0.5	0.2	0.3	0.0	0.4	-0.4	0.4	0.2	0.2	0.2	0.0	0.2	0.4	0.1	0.3	3.5	0.4	3.1	0.3	0.2	0.1
Final Cooler CT cold well, pH12	800	160	10	29	2.0	0.2	0.2	0.0	0.2	0.4	-0.2	0.3	0.2	0.1	0.3	0.0	0.3	0.2	0.1	0.1	2.9	0.4	2.5	0.2	0.2	0.0
Tar Decanter condensate, pH2	150	138	10	507	0.5	0.1	0.0	0.1	1.7	0.2	1.5	2.4	0.3	2.1	0.5	0.3	0.2	0.5	0.1	0.4	5.2	0.4	4.8	0.2	0.3	-0.1
Tar Decanter condensate, pH12	150	138	10	26	2.0	0.3	0.0	0.3	0.1	0.2	-0.1	0.5	0.3	0.2	0.3	0.3	0.0	0.4	0.1	0.3	1.4	0.4	1.0	0.4	0.3	0.1
Bio. plant sludge, pH7	450	45	10	56	5.0	3.2	0.0	3.2	0.9	0.0	0.9	1.1	0.0	1.1	0.4	0.0	0.4	0.1	0.0	0.1	5.3	0.1	5.2	0.6	-0.1	[illegible]

NOTES: [(a)] Total GRAV mass in an LC cut = [Corrected Grav mass] x [2.5 for LC1 (2.0 for LC2-LC7)]. GRAV mass is ratioed back to original sample by multiplying GRAV mass in an LC cut by (Concentrate volume/Volume put on column).

[(b)] Total canister rinse samples taken to dryness and GRAV determined (Concentrate GRAV). Sample placed on column was weighed amount of GRAV material presented in "Volume on column" column in table.

[(c)] Sample spilled.

APPENDIX B

COST ESTIMATES FOR BYPRODUCT RECOVERY PLANTS

APPENDIX B

COST ESTIMATES FOR BY-PRODUCT RECOVERY PLANTS

Under subcontract to the Research Triangle Institute, The Wilputte Corporation, Murray Hill, N.J., prepared capital cost estimates for selected by-product plant processes, also providing utilities, manpower, and chemical utilization estimates. The Wilputte estimates are for turnkey projects in third quarter 1977 dollars, and do not include working capital. They are factored from plants built or estimated by Wilputte Corporation over the past few years. All of these by-product plant processes are based on a coke oven gas flow of 1,416,000 m^3/day (50,000,000 scf/day), which corresponds to roughly 4,160 Mg coke/day (4,580 tons/day). Limited (factor of 2) extrapolation of the capital costs to different capacities, using a 0.6 factor, is considered reasonably valid by Wilputte. An exception is the anhydrous ammonia plant, which has such a small capacity that doubling or halving its capacity would not significantly change the capital cost.

Costs of the utilities, chemicals, and manpower were estimated by RTI. Chemical prices were obtained from the Chemical Marketing Reporter.[70] Where the prices of by-product plant grades were not available, as for phenol, the petroleum-based prices were discounted by 50 percent.

Utilities costs were escalated to the third quarter of 1977 from those presented by Massey and Dunlop.[33] Twenty percent escalation was assumed.

Operator manpower was estimated at $9.00/hr, with benefits at 30 percent of salary, which totals to $102,500/yr per working post.

Capital costs were put on an annual basis by amortizing over a 20-year life at 9 percent interest.

(1) PHENOL REMOVAL PLANT

Phenol extraction from ammonia liquor with coke oven light oil, followed by reaction with sodium hydroxide to produce sodium phenolate for sale

Capacity: approximately 433,400 l/day (114,500 gal/day) ammonia liquor, producing 1,400 l/day (370 gal/day) of sodium phenolate

Design Removal: 3,500 ppm phenol incoming to 5- ppm

Factored From: Plant handling 250,000 gal/day, built in 1969

Capital Cost of Plant:	$1,600,000

Operating Costs, Single Day Basis	$/day
Daily Cost of Capital	480
Electricity [728 kwhr/day @ $.025/kwhr]	18
Steam (150 psig) [41,678 lbs/day @ $4.25/1,000 lbs]	177
Cooling Water [158,285 gal/day @ $0.03/1,000 gal]	5
Caustic Soda, 100% [2,519 lbs/day @ $315/ton]	397
Labor [0.25 man @ $102,500/yr per post]	70
Maintenance [3 percent of capital cost annually]	132
Total Operating Cost	$1,279
Phenol Credit [370 gal/day x 8.9 lb/gal x $.105/lb]	346

(2) ALTERNATE PHENOL REMOVAL PLANT

Activated Sludge treatment and clarifier-thickener.

Capacity: approximately 433,400 l/day (114,500 gal/day) ammonia liquor

Design Removal: 3,500 ppm phenol incoming to less than 1 ppm

Factored From: Plant of 230,000 gal/day, estimated in 1975

Capital Cost of Plant	$1,900,000

Operating Costs, Single Day Basis	$/day
Daily Cost of Capital	$570
Electricity [44 kwhr/day]	1
Steam - 150 psig [13,333 lbs/day]	5
Steam - 15 psig [5,370 lbs/day @ $2.12/1,000 lbs]	11
Make-up water [116,665 gal/day @ $.06/1,000 gal]	7
Phosphoric Acid, 75% [14 gal/day @ $1.50/gal]	21
Labor [0.1 man/shift]	28
Maintenance [3 percent of capital cost annually]	156
Total Operating Cost	$851/day

(3) AMMONIA STILLS

Facility includes both free and fixed stills, using lime in fixed still. Included are dephlegmator, lime handling, storage, and slaking facilities, concrete lime settling basin, two ammonia liquor storage tanks (24 hrs each), pumps and auxiliaries.

Capacity: 18,200 l/hr (4,800 gal/hr) to 27,200 l/hr (7,200 gal/hr to allow for peaks.

Design Removal: 6 g/l total ammonia to 0.015 g/l in effluent. Plant "recovers" 1,020 kg ammonia per hour.

Factored From: 5,000 to 7,500 gal/hr plant estimated in 1976.

Capital Cost of Plant: $2,280,000

Operating Costs, Single Day Basis	$/day
Daily Cost of Capital	684
Steam - 18 psig [231,264 lbs/day @ $2.12/1000 lb]	490
Make-up Cooling Water [751,680 gal/day @ $.06/1000 gal]	45
Labor [0.1 man/shift]	28
Total	$1,247/day

(4) AMMONIUM SULFATE PLANT WITH VACUUM CRYSTALLIZER

Absorption of NH_3 in sulfuric acid, vacuum crystallizer, salt drying, and storage facilities.

Capacity: 1,416,000 m^3/day (50,000,000 scf/day) coke oven gas (say 64 tons/day sulfate)

Design Removal: 10.6 g/m^3 of ammonia on inlet, 0.11 g ammonia/m^3 coke oven gas on outlet.

Factored From: 95 ton/day plant (74,000,000 scfd gas) estimated in 1976.

Capital Cost of Plant: $8,050,000

Operating Cost on Daily Basis	$/day
Daily Cost of Capital	2,416
Electricity [3,526 kwhr/day]	88
Steam - 160 psig [78,840 lbs/day]	335
Steam - 18 psig [105,120 lbs/day]	223
Sulfuric Acid, 100% [99,782 lbs/day @ $50.00/ton]	2,494
Labor [0.1 man/shift]	28
Maintenance [3 percent of capital cost annually]	662
Total	$6,246/day
Credit for Ammonium Sulfate [64 tons/day @ $65/ton]	$4,160.00/day

(5) ANHYDROUS AMMONIA PLANT

Facility using U.S. Steel Phosam® process for production of anhydrous ammonia.

Capacity: 12 tons/day anhydrous ammonia

Design Removal: 7.8 g ammonia/m^3 coke oven gas to 0.1 g ammonia/m^3 gas (1,416,000 m^3/day gas)

Factored From: Plant sold in 1973 for 100,000,000 scfd gas (24 tons/day ammonia). Checked against facility handling 45,000,000 scfd gas estimated in 1976.

Capital Cost of Plant: $2,740,000

Operating Costs, Single Day Basis:	$/day
Daily Cost of Capital	822
Electricity [2,930 kwhr/day]	73
Steam - 250 psig [280,000 lbs/day @ 5.00/1,000 lbs]	1,400
Steam - 18 psig [280,000 lbs/day]	594
Make-up Cooling Water [1,108,800 gal/day]	67
Phosphoric Acid (100%) [185 lbs/day @ $20.67/100 lbs]	38
Caustic Soda (100%) [241 lbs/day]	38
Labor [0.1 man/shift]	28
Maintenance [3 percent of capital cost annually]	225
Total	$3,285/day
Credit for Anhydrous Ammonia 12 tons/day @ $130/ton	$1,560/day

(6) INCINERATION OF WET AMMONIA VAPOR OR ANHYDROUS AMMONIA

Capacity: Sized to add to anhydrous ammonia process above; i.e., 12 tons/day anhydrous ammonia

Capital Cost of Plant: $200,000

Operating Costs, Single Day Basis:	$/day
Daily Cost of Capital	60
Electricity [358 kwhr/day]	9
Coke Oven Gas [1,370,182 scf/day @ $1.00/1000 scf]	1,370
Labor [0.1 man/shift]	28
Maintenance [3 percent of capital cost annually]	16
Total	$1,483/day+Air

(7) WASH OIL TYPE FINAL GAS COOLER

Final gas cooling and naphthalene removal using petroleum wash oil, with bleed-off of naphthalene rich oil to light oil recovery plant.

Capacity: 1,416,000 m^3 gas/day (50,000,000 scf/day)

Design Removal of Naphthalene: to 45-90 mg/m^3

Factored From: 74 MM Scfd gas plant estimated in 1976.

Capital Cost of Plant: $2,360,000

Operating Costs, Single Day Basis	$/day
Daily Cost of Capital	708
Electricity [3,629 kwhr/day]	91
Wash Oil [variable]	
Labor [0.25 man/shift]	70
Maintenance [3 percent of capital cost annually]	194
Total	$1,063/day

(8) VACUUM CARBONATE PLANT

Vacuum carbonate plant for H_2S removal with HCN stripping and Claus Sulfur Recovery Unit.

Capacity: 1,416,000 m^3 gas/day (50,000,000 scfd gas)

H_2S Removal: to 1.12 g/m^3 (50 gr/100 scf)

Factored From: Plant handling 100 MM Scfd gas estimated in 1973.

Capital Cost of Plant: $5,040,000

Operating Costs, Single Day Basis	$/day
Annual Cost of Capital	1,513
Electricity [4,854 kwhr/day]	121
Steam - 160 psig [178,704 lbs/day]	759
Steam - 18 psig [394,200 lbs/day]	835
Make-up Water [146,800 gal/day]	9
Sodium Carbonate (100%) [18,835 lbs/day]	1,039
Labor [0.1 man/shift]	28
Maintenance [3 percent of capital cost annually]	414
	$4,718/day

(9) HOLMES-STRETFORD PLANT FOR H_2S REMOVAL INCLUDING FIXED SALTS RECOVERY UNIT

Capacity: 1,416,000 m^3 gas/day (50,000,000 scfd gas)

Design, Gas In:	10.1 g H_2S/m^3 and 0.45 g/m^3 organic sulfur expressed as H_2S.
Design, Gas Out:	total sulfur expressed as H_2S, less than 35 grains/100 scf. 0.79 g/m^3 (35 gr/100 scf)

Capital Cost of Plant:	$9,000,000

Operating Costs, Single Day Basis:	$/day
Daily Cost of Capital	2,701
Electricity [27,315 kwhr/day]	683
Steam - 180 psig [34,793 lbs/day]	148
Steam - 15 psig [573,248 lbs/day]	155
Make-up Water [329,616 gal/day]	20
Coke Oven Gas [380,889 scfd]	381
ADA [175 lbs/day]	?
Vanadium [1.5 lbs/day]	?
Citric Acid [175 lbs/day @ $.58/lb]	102
Labor [1.25 man/shift]	351
Maintenance [3 percent of capital cost annually]	740
Total	$5,281/day